Corrosion

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CORROSION CONTROL
PROTECTS INDUSTRY
NATIONAL ASSOCIATION OF CORROSION ENGINEERS

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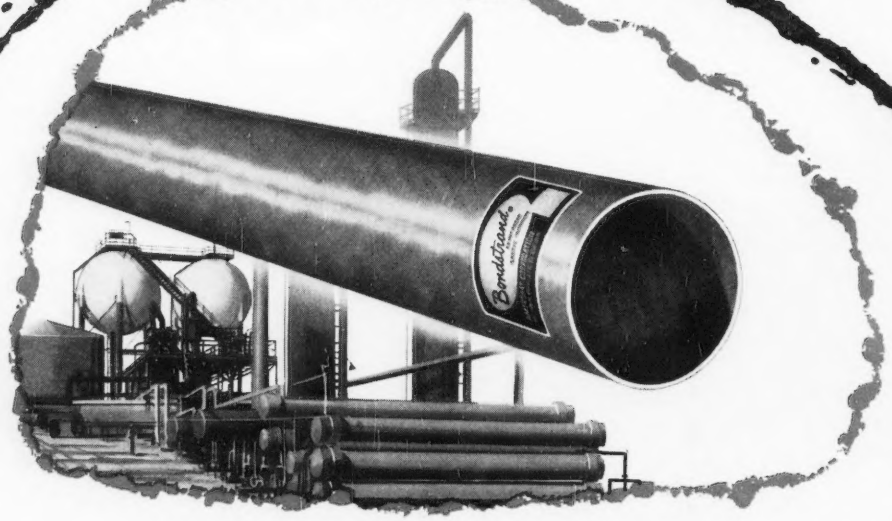
No. 9



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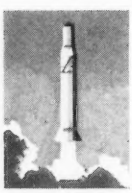

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another
TRETOLITE SERVICE
report

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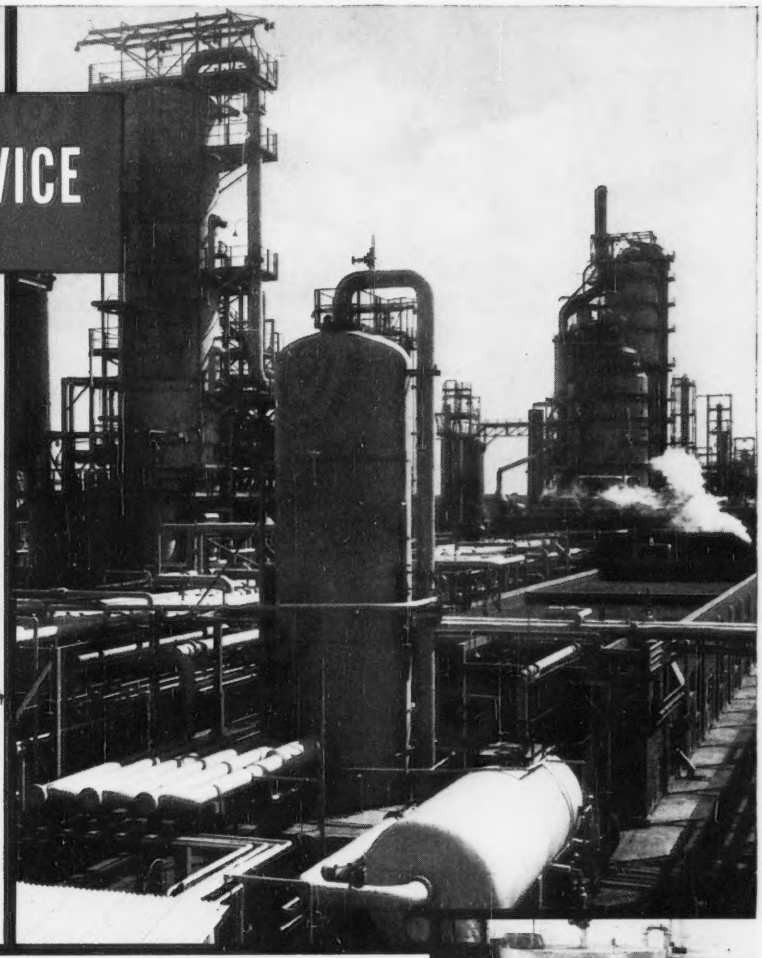
Corrosion Inhibitor permits low pH operation in refinery's crude unit overhead system



OHIO OIL COMPANY GETS EFFECTIVE CORROSION CONTROL, BETTER PRODUCT QUALITY AT REDUCED COST

An outstanding performance record compiled over a five-year period in Ohio's refinery at Robinson, Illinois, proves the feasibility of low pH operation augmented by KONTOL* Corrosion Inhibitors.

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Low pH operation supported by KONTOL corrosion control might offer important advantages for your refining facilities. Ask the Man in the Red Car to explain this program, or write . . .

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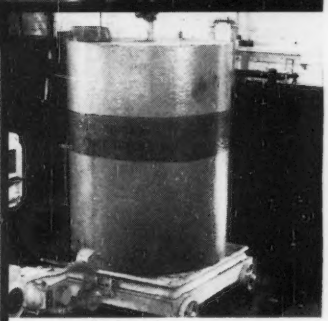

Facilities such as this one for Kontol injection at various points are part of over-all corrosion control program at Ohio Oil Company's Robinson, Ill., refinery.

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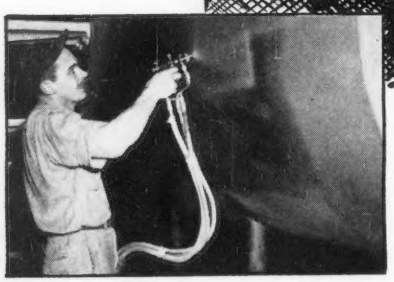

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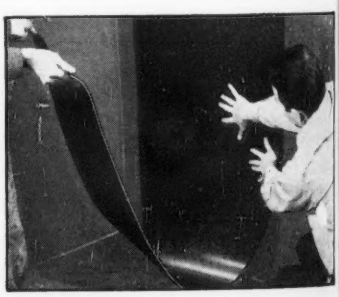

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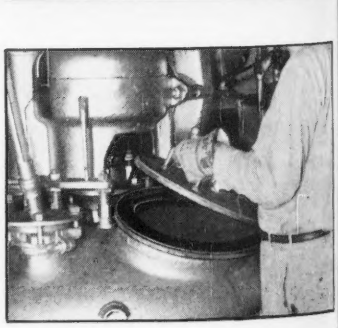

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This Month in Corrosion Control . . .

CATHODIC PROTECTION of glass-lined water heaters is more complicated than the simple addition of an anode. Some of the problems involved in designing protection and estimating current demand for glass lined heaters are covered in an article beginning on Page 9. A novel thermoelectric current source is described also.

UTILITY GAS LINES (8-inch) can be coated and protected cathodically for about 63 cents a foot. Cathodic protection alone costs 21 cents a foot. See these data and others on Page 20.

WATER TURBULENCE increases galvanic cell corrosion. A short item on Page 22 gives a case history on condenser cooling equipment.

HONEYCOMB STRUCTURES used to give strength and light weight to aircraft present some challenging problems in corrosion control. How tests were devised to give reliable data are described on Page 24.

WELDED STEEL PIPING used for pumping columns expected to last 20 years failed in three when exposed to South African mine waters. A complete investigation was made to determine the cause and the solutions adopted are given. Coatings are being tested. See Page 32.

AIR-CONDITIONING cooling systems on large metropolitan buildings are susceptible to corrosion from air contaminants. A report on Page 37 shows what sulfur dioxide can do to cooling towers in 18 months.

RUSSIAN LITERATURE on corrosion topics available in this country are listed on Page 40, together with references to prior articles on this subject published in CORROSION.

ALUMINUM PIPE buried bare without cathodic protection gave six years' service before pitting from the outside caused a failure. More about this report on pipe handling sour gas will be found on Page 91.

STRESS CORROSION CRACKING of austenitic stainless steels and other materials was studied using equipment to record automatically electrochemical potential changes and the sound made by the cracking material. Reports on tests supporting the electrochemical mechanism of this phenomenon are reported beginning on Page 93.

HYDROGEN PERMEATION through Type 446 stainless steel at 2150 F is materially affected by an oxide film on the surface of the material. When the oxide could not be replenished, its beneficial effect was largely destroyed by emerging hydrogen. See Page 102.

CORROSION RESISTANCE of Type 347 stainless steel can be affected by the variations of constituents within the compositional limits. Field tests indicate that the influence of compositional elements varies with environment. Numerous tabulated data and charts are included in an article beginning on Page 105.

SOIL BACTERIA have a significant effect on the life of coatings on buried pipelines which are cathodically protected. Bacterial populations are higher next to pipe than in undisturbed soil. Numerous data on conditions in pipeline ditches are reported in a fully illustrated article starting on Page 114.

INTERFERENCE PROBLEMS encountered between cathodic protection currents and railroad signal systems are reviewed and some corrective measures reported. See Page 121.

HOW DOMESTIC WATERS corrode galvanized and black iron, aluminum and copper pipe is described in an NACE report beginning on Page 125. Tests were made with 30 different hot and cold waters. This experiment covered a two-year exposure period and, while exhibiting some deficiencies, showed among other things that black steel was unsatisfactory for normal service use.

ALUMINUM-COPPER COUPLES produced the most corrosion in laboratory tests of hypereutectic aluminum-silicon alloys such as are found in automobile engine cooling systems. Inhibitors were found which reduced corrosion to negligible proportions. See Page 129.

AIR-CONTAMINATED LITHIUM will selectively remove chromium from Type 304 stainless steel at 800-1500 F. See Page 140.

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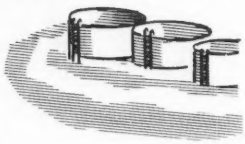

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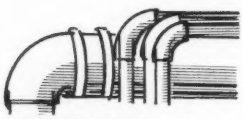

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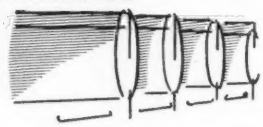

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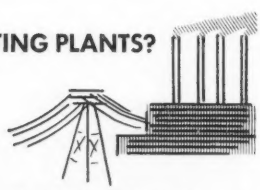

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Facts and Numbers Are Essential to Success

AFTER FINANCING a billion dollars worth of business, a large financing company has found two characteristics of a manufacturing corporation that are indicative of success. This company believes you can predict a firm's future—regardless of its size and assets at the moment—by the degree of attention it pays to facts and numbers.

In deciding whether or not to finance a company, this financing agency looks for management's disposition to worry about facts. For example, if a decision is made to produce a new product, is the decision based on a market study, a fair estimate of production and sales costs and other essentials? Likewise, is management concerned about numbers? For example, does it concern itself about whether or not each of its products is making a profit?

While these two considerations seem so elementary that it is hard to imagine a business functioning at all without them, apparently many businesses try to do just that.

These same considerations likewise are important to a company that wants to do something about its corrosion losses. Is management interested in the fact of corrosion? Is it willing to recognize that corrosion exists? Is it willing to listen to its own corrosion control engineer when he tries to show how money can be saved by paying attention to corrosion control problems the company has?

Will management recognize the extent to which corrosion losses eat into net profits? How much the reputation of the company's products may be adversely affected when they fail because the consequences of corrosion were ignored during design and manufacturer?

Corrosion is not something which, when ignored will go away. It is not something which rises and falls in consonance with business activity, stock market prices, political events, interest rates. It cannot be talked out of existence. It cannot be calculated away. It cannot be stopped by legislation.

It is one result of man's subservience to the laws of thermodynamics.

It is a wise management that recognizes the **fact** of corrosion, and then proceeds to determine its **quantity.** Once the quantity is known, a calculated risk can be taken to ignore it, or a decision can be made to control it. On the whole, engineering logic favors prevention. Prevention succeeds best when it is part of initial planning. It is far better to build a fireproof structure than to rely on an efficient fire department.

NACE has been busy this last 15 years gathering the facts for those companies that want to do something about their corrosion losses. These facts are available in a number of ways, and at a very nominal cost indeed compared to their possible benefit. But the association cannot itself do anything directly for the companies. The benefits of NACE activity are realized only after the company itself decides to do something.

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Solving Design Problems for Cathodic Protection of Glass-Lined Domestic Water Heaters*

H. C. Fischer
Thermo-Craft Corp.
New York, N. Y.

Abstract

Factors important in designing a cathodic protection system for glass lined domestic hot water heaters are considered. Method by which bare areas of single coated glass lined tanks can be calculated is explained, and comparisons are made between calculated values and those obtained by tests on tanks under protection. Instruments for making these tests and techniques are illustrated and described.

Design data relevant to required current densities are considered with respect to platinum clad tantalum and platinum plated titanium anodes. Regulations of Underwriters' Laboratories concerning accumulated gas from cathodic protection systems are weighed against test results and the volume of gas actually produced is measured and analyzed.

Design criteria and details for rectified current used in systems applied to electrically heated tanks are given. Details of a thermoelectric generator for use with gas fired tanks are given. This generator produces sufficient current to protect a well-lined tank in the highest resistivity water likely to be encountered.

5.2.3

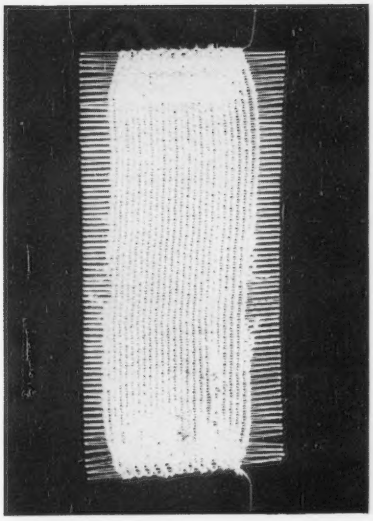

Figure 6—Thermo-electric fabric, used as a source of energy for tank cathodic protection system. Wires are Copel X and Chromel P. Fabric fill is fiberglass. Glass has been removed from areas near weld junctions. Electromotive output is the sum of the forces created at the weld junctions by the difference in temperature of the metals.

THE TREND in the water heater industry toward extending ten and fifteen year tank warranties has focused attention on the means of providing an assured long life for water heater tanks no matter in what area they are installed. Production water heaters now have shortcomings of which the public is becoming increasingly aware as witnessed by the article in September, 1958 issue of The Kiplinger Magazine "Changing Times" entitled "Why Water Heaters Die Young."

The use of galvanized tanks is rapidly diminishing because of their short life in many waters.[1] There are some waters in which galvanizing provides no protection at all. Heated waters which are aerated and contain the bicarbonate ion may cause zinc to be cathodic to iron[6] and thus help corrode the iron rather than protect it.

Glass tank lining costs approximately the same as galvanizing and is rapidly becoming dominant in the water heater industry. However, glass lined tanks present their own problems in corrosion control.

All porcelain or glass linings are imperfect and have many small holes or holidays. Sudrabin has shown that the open circuit potential between iron in an air free environment (anode) and magnetic iron oxide (mill scale, rust), in an aerated environment (cathode) exceeds one volt.[7] This means that holidays which reach down to the magnetic iron oxide-rich porcelain layer are more cathodic than copper and require more current for polarization.

The electrical conductivity of the magnetic iron oxide-rich porcelain layer is not known, but it is known that "copperheads," which are a manifestation of this layer on the surface, will conduct electricity well.

Sources of Energy Explored

The corrosion problem in hot water heater tanks can be approached from the standpoint of the amount of energy required for a cathodic protection system to arrest tank corrosion.

The amount of energy required to prevent corrosion in various types of tanks is approximately as follows:

1. A black iron tank would require approximately 20 ma per sq. ft. A 15 sq. ft. tank with an anode

(Continued on Page 10)

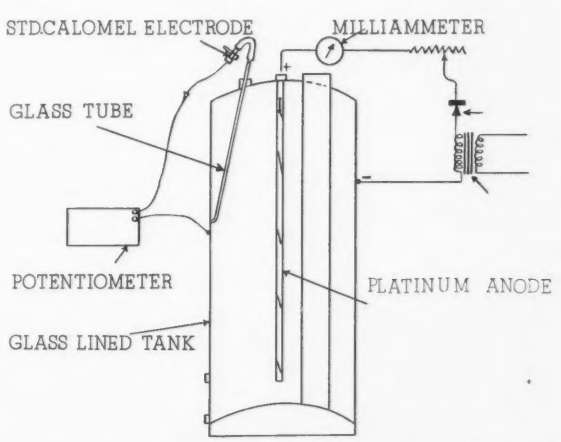

Figure 1—Showing the method of using a glass tube calomel reference half cell to plot the voltage at various points inside a tank.

*Revision of a paper titled "Design Problems in Applying Permanent Cathodic Protection to Glass-Lined Water Heaters" presented at the Northeast Region Conference, Baltimore, Md., October 5-8, 1959.

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Water Heaters—

(Continued From Page 9)

operating at 5 volts would require about 1½ watts to be polarized in a typical medium conductivity water.

2. A similar galvanized tank would require only 4 ma sq. ft. at approximately 4 volts. This would result in a consumption of ¼ watt per hour to prevent corrosion.

3. In a glass lined tank the amount of bare area has been reduced to something less than 2 square inches. Approximately 3 ma will adequately protect a good glass lined tank. An anode providing this current operates at approximately 3 volts. This means an energy consumption of .009 watt. Thus it can be seen energy requirements to prevent corrosion of a glass-lined tank are much less than for other types.

Energy required to prevent corrosion of a glass lined tank varies with the temperature, pressure, resistivity and composition of water. As the temperature of the water increases the energy required to prevent corrosion increases, largely because depolarization takes place much more rapidly as the water gets hotter. As pressure is increased the power required to protect a tank also goes up. High resistance waters require more power to prevent corrosion because of the increased IR drop, and also because of the poorer throwing power of an anode in high resistance waters. Poor throwing power requires much more current to give all areas minimum current necessary to prevent corrosion.

Calcareous salts deposits reduce the amount of energy required; whereas, 3 ma is required to prevent corrosion in a tank in New York, less than 1 ma will prevent corrosion in a glass lined tank in Cleveland.

Copper Ions Harmful

Small amounts of copper ions picked up in the copper plumbing used in most modern homes greatly affects the life of magnesium and zinc anodes because it causes the energy to be wasted on local cell corrosion. Copper in the water deposits on the anode or on the interior of a galvanized tank and forms a cathode area. Soon a vigorous corrosion cell is set up and the consumption of zinc or magnesium necessary to polarize these small copper cathodes consumes the anode, thus shortening its life. In the case of nonsacrificial powered anode the heavy metal ions such as copper have no effect on the energy level of the system.

Electrical Properties of Glass Lining

Glass lining does more than reduce the area to be protected. It increases the throwing power of the protective current by providing a surface resistance many times greater than the polarization film found in a cathodically protected bare tank. In addition it reduces the amount of current required so that in many well coated glass tanks less than 5 milliamperes is sufficient.

In considering the design of a cathodic protection system for domestic glass lined water heater tanks, one of the first questions to be answered is "What current will be required for a glass lined tank?"

If the glass lining were perfect it wouldn't take **any** current. C. J. Bergeron of the University of Illinois reports resistivity of ground coat enamels to be in the order of 10^{14} ohms cm. Perfect ground coat when considered at normal thicknesses of 0.004 inch to 0.006 inch would have a resistance of 10^{12} ohms/cm². However, measurements of single-coat tank linings indicate surface resistance to be much lower. This low resistance is accounted for by holidays in the coating. The number of holidays to be found—and their extent—is one of the questions to be answered.

Results of Tests Given

Table 1 shows a summary of the results obtained from several tests on five single coated glass lined tanks of varying sizes, design, and manufacture, in four different waters of varying resistance. Data apply to tanks with single coat porcelain linings. Greatly improved values can be expected from double coated tanks.

Resistance values shown in Table 1 were obtained by measuring the alternating current flow. It is necessary to use alternating current to get valid resistance values because with direct current the anode-to-cathode potential and the polarization potential at the cathode make a true resistance reading difficult. After obtaining the overall resistance from anode-to-tank from the formula $R = E/I$, it is necessary to **measure or calculate** that portion of the resistance that is due to the water. In a cylindrical vessel diameter D with concentric anode of (d) diameter the following formula applies:

$$R_w = \frac{\rho}{2\pi L} \log_n \frac{D}{d} \qquad (3)$$

ρ is expressed in ohm centimeters and anode length L is also in centimeters.

(Continued on Page 12)

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Water Heaters—

(Continued From Page 10)

The expression D/d is dimensionless, therefore, the diameter of the tank in inches can be divided by anode diameter in inches to obtain this value.

The voltage drop due to resistance of the water can be **measured** by probing the inside surface of the tank with a metal rod insulated except for the tip. Because the voltage drop is proportioned to the resistance, the voltage reading at the water-to-porcelain interface gives a means of calculating the resistance of the porcelain coating.

From Table 1 there is fair agreement generally between calculated and measured resistance. By subtracting the resistance of the water from the total resistance, the resistance due to the enameled surface of the tank can be obtained. Rather than the large resistance reported by Professor Bergeron, these tests show that resistance due to the enameled surface is nominal.

Total surface resistance also varies with the resistivity of the water used in the test, (note tanks A and B.) This is as would be expected, however, because the holidays in the glass coating are filled with the electrolyte and, therefore, their resistance is a function of its resistance. Therefore, the problem of calculating the amount of bare area in the glass coating is necessary.

TABLE 1—Data on Single-Coated, Glass-Lined Domestic Water Heaters

Tank	Degrees F Test	Water Resistivity Ohm/CM		Anode-To-Tank Resistance Ohms	Total Tank Surface Resistance		Bare Area Cm^2/ sq. ft.	Size, Inches		Inside Area Sq. Ft.
		70 F	Test Temp.		Calculated	Measured		D	Sheets	
A	70	8,200	8,200	108[3]	72.5	....	0.055	18	48	20.6
A	120	18,100	12,100	407[1]	174	178	0.332 0.339	18	48	20.6
B	70	8,200	8,200	118[3]	72	76.5	0.0675 0.0715	16	36[4]	15.9
B	120	18,100	12,100	347[1]	127	160	0.0475 0.0606	16	36[4]	15.9
C	140	18,100	10,500	300[1]	109	100	0.0686 0.075	12	48	14.0
D	70	3,100	6,700	214[3]	86.4	....	0.0488	16	36[4]	15.9
E	150	6,700	1,720	136[2]	76	72	0.0434 0.041	10 ⅝	20	5.5

[1] Pt. anode 0.011 D x 24 inches.
[2] Pt. anode 0.011 D x 12 inches.
[3] Copper anode 0.625 D x 40 inches.
[4] 3-inch flue.

Calculative Bare Area

Because all the tanks measured had a single coat of porcelain enamel lining of approximately the same thickness, a formula for calculating bare area assumes an average tank coating of about 0.004 inch. And, because ρ is expressed in ohm centimeters, it can now be expressed in ohms per square centimeter by dividing it by 0.394 (number of inches per centimeter) and multiplying it by the coating thickness 0.004 inch. For all practical purposes on single coated tanks this means dividing ρ by 100. The bare area of a tank, therefore is

$$A_b = \frac{\rho}{100} \times \frac{1}{R_s} \frac{1}{A}$$

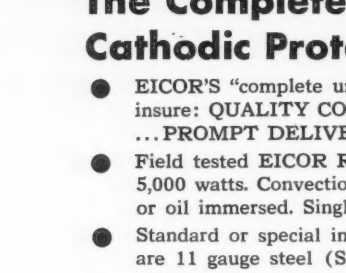
R_s = Total surface resistance

A = Area of tank in sq. ft.

This results in an expression of bare area in terms of square centimeters per square foot, which may be converted to square inches per square foot if one desired.

The areas are so expressed in Table 1. Although complete agreement is not obtained, the figures show remarkably uniform amounts of bare area considering that the tanks were manufactured by three different companies and that they were tested in four different waters varying in resistance from 3100 to 18,000 ohm centimeters.

The purpose of obtaining the values shown in Table 1 is to find a means of calculating the total anode-to-tank resistance in a commercial glass lined tank so that the proper resistors can be specified on the power supply. Using the above formulas a 22-inch diameter x 48 inch



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sheet, 80-gallon tank, with a 36 inch by 0.011 diameter platinum anode in 20,000 ohm centimeter water would have a total resistance of 381 ohms of which 117 ohms is the resistance of the coating (assuming bare area of 0.06 cm²/sq. ft.).

In a 1200 ohms/centimeter water the resistance of this tank would be 23 ohms of which 7 ohms would be due to coating. In designing a cathodic protection system current must be provided that will protect the tank in 20,000 ohm centimeter water and which will not overheat the rectifier in 1200 ohm centimeter water. Care must be taken to correct the above resistances for the temperature at which the water heater will be operated.

Conductivity of water increases approximately 2 percent for every degree C rise; thus 20,000 ohms centimeter water at 70 F becomes 11,250 ohms centimeter water at 140 F and 9100 ohms centimeter water at 180 F. Resistivity of water can be measured easily if one has a soil box or other similar apparatus used for measuring resistances of water and earth. If such equipment is not available, water resistivity can be estimated fairly well by the formula

$$R = \frac{625{,}000}{\text{Solids in ppm}}$$

Function of Tank Probe

The calculations given can be used to estimate the overall resistance and performance of a cathodic protection system in a glass lined tank, but it only gives a means of sizing equipment for a given tank. It is necessary in designing for proper cathodic protection to employ tank probe consisting of a calomel reference cell, glass tubing to act as a conductive bridge and a potentiometer capable of reading to .01 volt in the range of 0 to 3 volts. An anode, preferably cylindrical, and a milliammeter, rheostat and DC power source are also required. (See Figure 1.)

The tank is filled with water and current is impressed. The calomel reference cell is attached by means of a rubber tube to the glass tube probe, which is filled with a potassium chloride solution to act as a conductor. The end of the glass tube is drawn to a point so that the solution is not lost when the tube is removed from the tank, and so that it can register the voltage on the side of the tank at the exact point where the glass tube terminates. Different pieces of tubing can be bent to make it possible to reach all of the areas in the tank from the inlet or outlet hole.

One side of the potentiometer circuit is connected to the tank shell, and the other to the calomel cell. Care must be taken to see that very little current flows through the calomel cell and that all readings are made by the null method. When the potentiometer reads greater than —0.78 volts, a surface against which the glass tip is resting is protected against corrosion.[9] Voltages below —0.78 are not protected and voltages above —0.78 are protected against corrosion. It is best to probe the tank hot to get results as near service condition as possible.

Figure 2 shows the results of probing a poorly glass lined hot water heater tank. Points on Curve A in this tank were either bare or showed coatings only of iron rich porcelain which is electrically conductive. Points on Curve A did not reach protective potential even when 25 milliamperes was impressed upon the tank. Because the throwing power of an anode in high resistance water is poor, the bare areas are too extensive to be protected by a central anode. Points along Curve B, which is the sharp edge of the head, reached protective potential after 10 milliamperes was impressed. Points on Curve C were protected at all amperages. This is an area which always should be checked in any cathodic protection survey because it is difficult to throw current into this corner unless the glass coating is of good quality. Points on Curve D were on the sides of the tank and the glass-coated sheath of the heater. These surfaces are easy to protect and account for about 95 percent of the area of the tank.

(Continued on Page 14)

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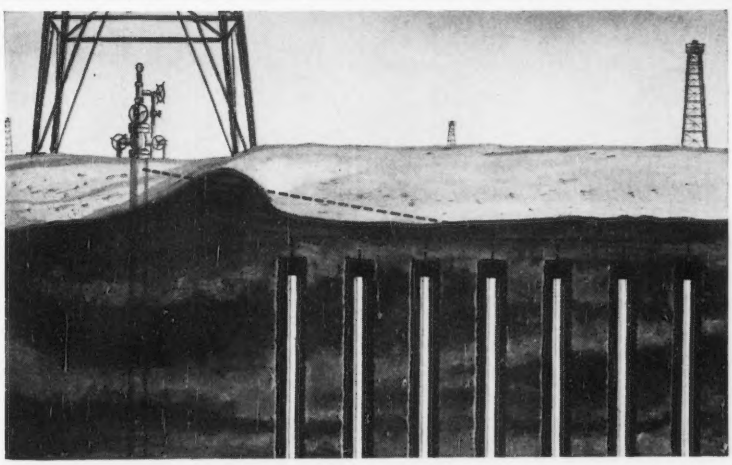

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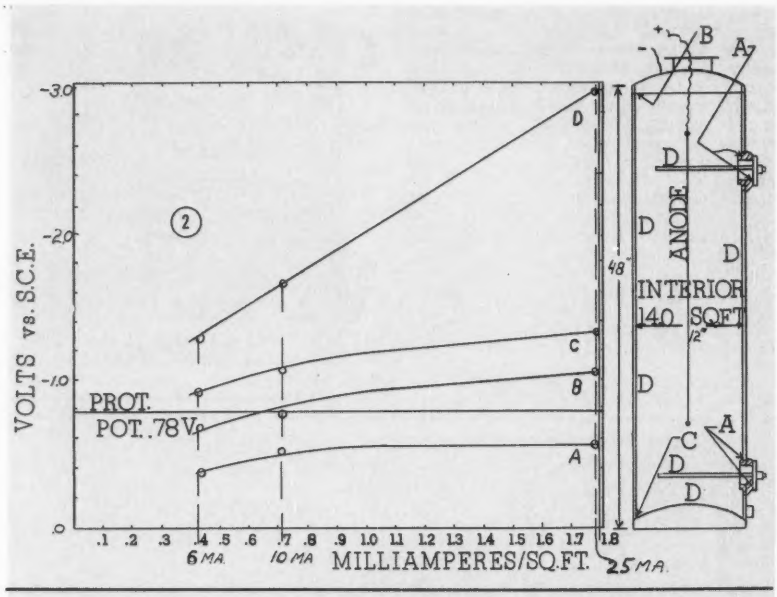


Figure 2—Protective current vs current density. Showing varitations in effective voltage at various locations in the tank. Tests made on poor quality glass lined tank, glass coated electric heater, 140 F, water resistivity 10,500 ohm/cm (18,200 ohm/cm at room temperature).

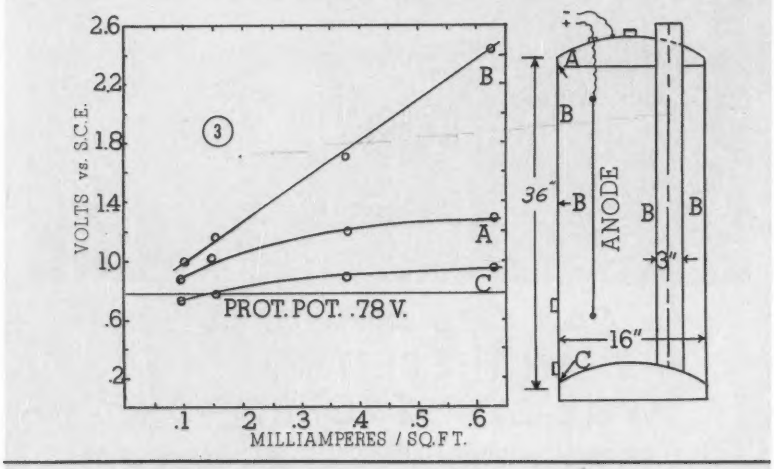


Figure 3—Protective potential vs current density at various locations on a glass lined tank of average quality. Temperature 120 F, water resistivity 12,100 ohm/cm (18,200 ohm/cm at room temperature). Interior area 15.9 sq. ft.

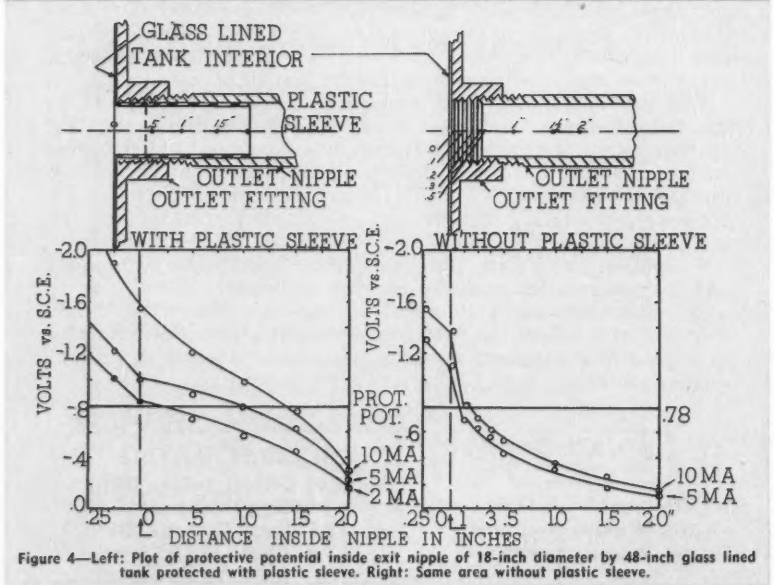


Figure 4—Left: Plot of protective potential inside exit nipple of 18-inch diameter by 48-inch glass lined tank protected with plastic sleeve. Right: Same area without plastic sleeve.

Water Heaters—

(Continued From Page 13)

Effect of Bare Metal Heaters

When bare metal electric heaters were installed in the tank, the surface of the metal heater consumed much of the protective current and depressed all values near the flange area. In electric water heaters it is necessary to use band heating elements or to electrically insulate the heating element from the tank to protect the tank surfaces which are in close proximity to the element. Other spots that must be checked are the inlet, outlet and drain connections.

Figure 3 represents an average glass lined gas hot water heater tank. Points along Curve C are the only critical areas in this tank outside of the inlet, outlet and thermostat connection. The sharp edges along Curve A are points at which protective potential is hard to attain because the glass coating is always thin and the iron-rich electrically conductive layer is exposed.

Figure 4 shows the effect of bare metal threads in the inlet, outlet and drain connections of a hot water tank.

Figure 4 also shows that the protective potential is lost one thread back from the inside of the tank. Such a connection is especially bad when connected with a brass nipple which makes a very unfavorable galvanic couple. Galvanized nipples would be better here because the galvanizing would act to protect the bare threads of the tank. This construction is especially vulnerable when the threads are cut in a neck extruded from the tank head material because the thread reduces by half the thickness of the metal.

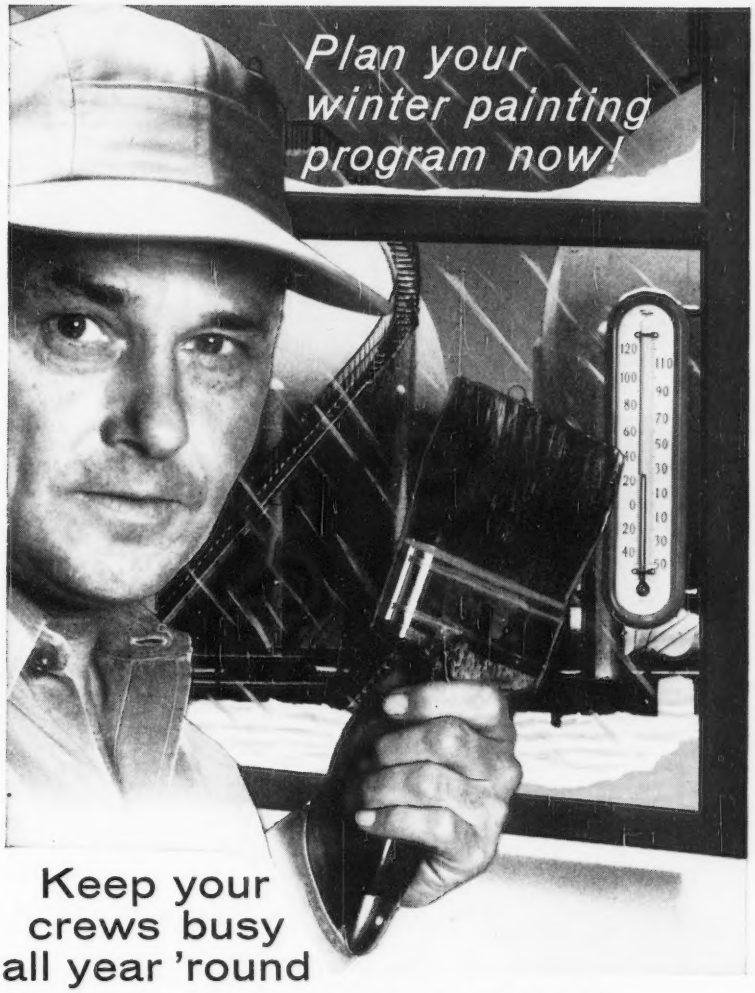
Figure 4 also shows how a plastic sleeve protects the interior of the tank nipple and the bare threads not covered by the threads of the nipple. This inexpensive linear polyethylene plastic sleeve effectively reduces the amount of current necessary to protect the inlet and outlet connections. The OD of the sleeve is an interference fit with the ID of the tapped threads in the spud, thus assuring a tight connection and preventing the sleeve from sliding through into the tank. Only 5 milliamperes were needed to maintain a protective potential one inch inside the plastic sleeve; 5 milliamperes were insufficient to protect the first thread in the bare nipple.

Effect of Water Resistance

Tests shown in Figures 2, 3 and 4 were conducted in water of high resistance compared to the average potable water found in the United States. Effect of the more conductive waters would be to flatten the curves, improve the throwing power and thus make it easier to protect bare areas.

In general the higher the resistivity of the water the more difficult it is to obtain cathodic protection. Thus, highly resistive water should be used in all probe testing of tanks in the laboratory where the purpose is to find spots most

(Continued on Page 16)



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Water Heaters—

(Continued From Page 14)

likely to corrode. High resistance water can be obtained from demineralizers or by using distilled water with the proper amount of local water added to adjust the resistance. Resistances of distilled water are much higher than will be found in service. The greatest resistances to be found in service usually will be about 24,000 ohm/centimeter at room temperature.

Problems of Anode Design

The least expensive anode material from an over-all standpoint is pure titanium. Titanium, tantalum and columbium are the so-called "valve" metals which form protective oxide films on their surfaces when operated as anodes. At low current densities of 0.5 to 1.0 amp. per sq. ft., titanium can operate satisfactorily as an anode. At this level the voltage drop across the oxide film does not exceed the 10 to 14 volts at which the film breaks down. Rapid corrosion follows such a film breakdown.[10]

A bare 0.051 by 30-inch titanium anode has been operated at 2 milliamperes per sq. in. for three months in a hot water tank at a voltage of 4.2 with no sign of anode corrosion. A similar anode of titanium around which has been wrapped a 0.002 by 0.008 by 36-inch platinum-clad tantalum ribbon operates at 2.5 volts at the same current level. (See Figure 5.)

The higher voltage required by the bare titanium anode presents no problem in the case of electric water heaters where a high voltage power supply can easily be provided. In the case of gas water heaters where the power is supplied by a thermo-electric generator, a platinum-clad ribbon wrapped around the titanium wire or platinum plated titanium wire must be used to keep the anode voltage as low as possible.

Recent tests with platinum plated titanium wire indicate that this combination will make a satisfactory impressed current anode for hot water systems. Large scale field trials are now under way using platinum plated titanium where the platinum plating is 10 to 20 microinches thick. (See Figure 5.)

Fluorocarbon sleeves are used to insulate the platinum faced titanium from the mounting fitting. The platinum faced titanium anode, in spite of its being made of exotic materials such as fluorocarbons, platinum, titanium and tantalum, is still the lowest cost anode on the market. A complete anode, including mounting fittings costs the water heater manufacturer between 75 cents and one dollar.

Providing Power for Systems

Providing power for the anode of an electric water heater is simple. Providing power for the anode of a gas water heater, however, is a real challenge, as discussed in later paragraphs.

From either of the 236-volt wires leading to an electric water heater to ground is 118 a-c volts. By interposing in series a silicon diode or other rectifying device and a dropping resistor, the half wave d-c current necessary to operate the anode can be obtained. In practice the resistance values lie between 10,000 and 5600 ohms for 5 to 10 ma current respectively.

Because the external resistance is high compared to the water resistance, a tenfold change in water resistance will affect the current flow very little.

The otherwise simple power supply problem for an electric water heater system is complicated by the fact that the Underwriters' Laboratories imposes restrictions on systems which may generate and accumulate dangerous amounts of hydrogen and oxygen during periods when no water is being used. Extended vacations are such periods.

Inside the water heater two reactions are taking place at the cathode:

$$1/2\,O_2 + H_2O + 2e \rightarrow 2\,OH^- \qquad (1)$$

$$H_2O \rightleftarrows H^+ + OH^- + e \rightarrow H^0 \rightarrow H_2\uparrow + OH^- \qquad (2)$$

In general Equation (1) will predominate at higher pressure and temperature because gas is being consumed and diffusion rates are greater at higher temperature. Equation (1) takes place at a lower voltage than Equation (2) and so would predominate at very low current levels.

Gas Output Is Tested

In order to determine the amount of hydrogen and oxygen produced, a 20-gallon tank (poor quality of glass lining) was operated at 10 ma current level for 14 days at 50 lb. per sq. in. line pressure without drawing any water. During this period no hydrogen and oxygen was accumulated, indicating that Equation (1) was predominating. The experiment was repeated with the same conditions except that the current was increased to 40 ma. After 9 days, 400 ML of gas was collected with the analysis given in Table 2.

This amount of gas, however, is only 20 percent of what would be expected according to Faraday's law. This indicates that 80 percent of the current went to satisfy Equation (1) and only 20 percent to the generation of hydrogen Equation (2). Much work remains to be done on the thermodynamic shift of these two equations with temperature and pressure.

TABLE 2—Analysis of Gas Produced

Oxygen	26.8 percent
Hydrogen	46.5 percent
Nitrogen	26.5 percent
Carbon Dioxide	0.2 percent

Tests are now underway to determine the effectiveness of a device to shut the anode off in case excess gas accumulates. Tests also are to be made to determine the actual hazard in a hot tank that has accumulated these gases at atmospheric pressure.

(Continued on Next Page)

Magnitude of Hot Water Heater Problem

It was estimated in 1954 that domestic hot water heaters ruined annually by corrosion were being replaced at a cost of $225 million.[1] No later estimate is available but it can be assumed that current replacement costs are more likely to be greater than this. The increased loss comes about because of the rapidly growing number of dwelling units equipped with heaters. Improved service life resulting from shifts to more corrosion resistant types cannot have been extensive enough to have affected losses materially.

Listed among the factors significant in the rate of corrosion damage to domestic hot water heaters are:

1. Composition of the water.
2. Temperature and pressure under which the tank is operated.
3. Rate of flow water through the tank.
4. Galvanic action from nonferrous metal fittings.
5. Kind and quality of the barrier coating inside the tank designed to prevent corrosion of the base metal.
6. Kind of base metal used. (Tanks made of Monel and copper have extended service lives in most environments.)
7. Design characteristics of the tank.

The necessity for cathodic protection of domestic hot water has been recognized for many years. A report on the need for and means of protecting the heaters was published in CORROSION in 1952.[2]

(1) William N. Brinker, Porcelain Enamel Institute. A speech delivered at the Mid-Year Divisional Conference, Porcelain Enamel Institute, Chicago, May 12-14, 1954.

(2) W. A. Deringer and F. W. Nelson. A Field Investigation of Cathodic Protection in Glass-Lined and Galvanized Water Heaters. CORROSION, 8, No. 2, 57-64 (1952) Feb.

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Thermoelectric Power Sources

Gas water heaters require a self contained power supply to provide the current for the cathodic protection system. This energy source must be capable of producing enough voltage to overcome the polarized iron-to-platinum cell voltage of approximately two volts, plus the IR drop required to make the necessary minimum current pass through the water in the worst possible case. Generally this means that 4 volts must be applied to the anode when minimum current is flowing.

Approximately 3 ma minimum current is required to protect a New York City tank which contains a typically high resistant water. To be safe, the system is being designed to provide a minimum of 5 ma in the worst case. This means, with 4 volts at the anode and 5 ma flowing, 20 milliwatts of effective power is required. A thermoelectric generator of 200 ohms internal resistance would require minimum open circuit voltage of 5 volts.

It is possible to obtain from Copel X-Chromel P thermocouples approximately 35 millivolts per couple with an 800 F Delta-T. It follows that 144 thermocouples are required to produce the 5 volt minimum open circuit voltage.

A practical thermoelectric generator of this kind is made by the author's company. (See Figure 6.) In this device the Copel and Chromel wires form the warp of the fabric and fiberglass forms the fill or woof. This fabric is woven on a Jacquard loom in such a manner that the thermopile can be automatically welded and cut from the woven fabric.

The thermopile is insulated, folded and sealed in a 23 percent chromium stainless steel outer cover and mounted so that it can be heated by 700 Btu pilot.

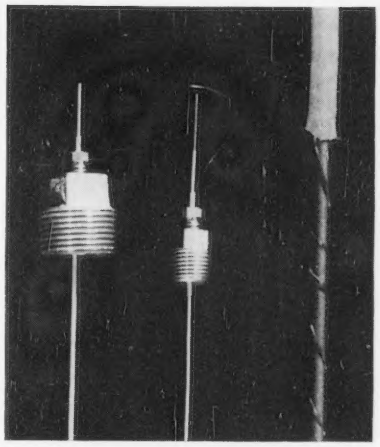

Figure 5—Left to right: Platinum plated titanium anode, two configurations, (approximately full size); right, platinum clad tantalum ribbon wound around 0.032 titanium wire (approximately 4X).

Tests on thermoelectric generators of this type indicate that the junction protection against oxidation must be improved to assure 10-year minimum life. These improvements are being made.

Conclusions

From the work done to date, it is felt that in commercial glass-lined water heater tanks, initial corrosion protection is possible with 5 milliamperes of cathodic current.

Anodes made from platinum clad tantalum ribbon wound around titanium wire appear to be effective and durable.

A thermoelectric generator is capable of providing the power necessary to provide cathodic protection for glass-lined gas water heaters.

Plastic sleeves inserted in the inlet and outlet connections of the tank improve the protective potential in and near these areas.

Single coat porcelain enameled tanks have an equivalent of 0.02 to 0.09 square centimeters per square foot of holidays or bare areas.

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10. J. B. Cotton. *Platinum Metals Review*, 2, No. 2, 45-47 (1958) April.

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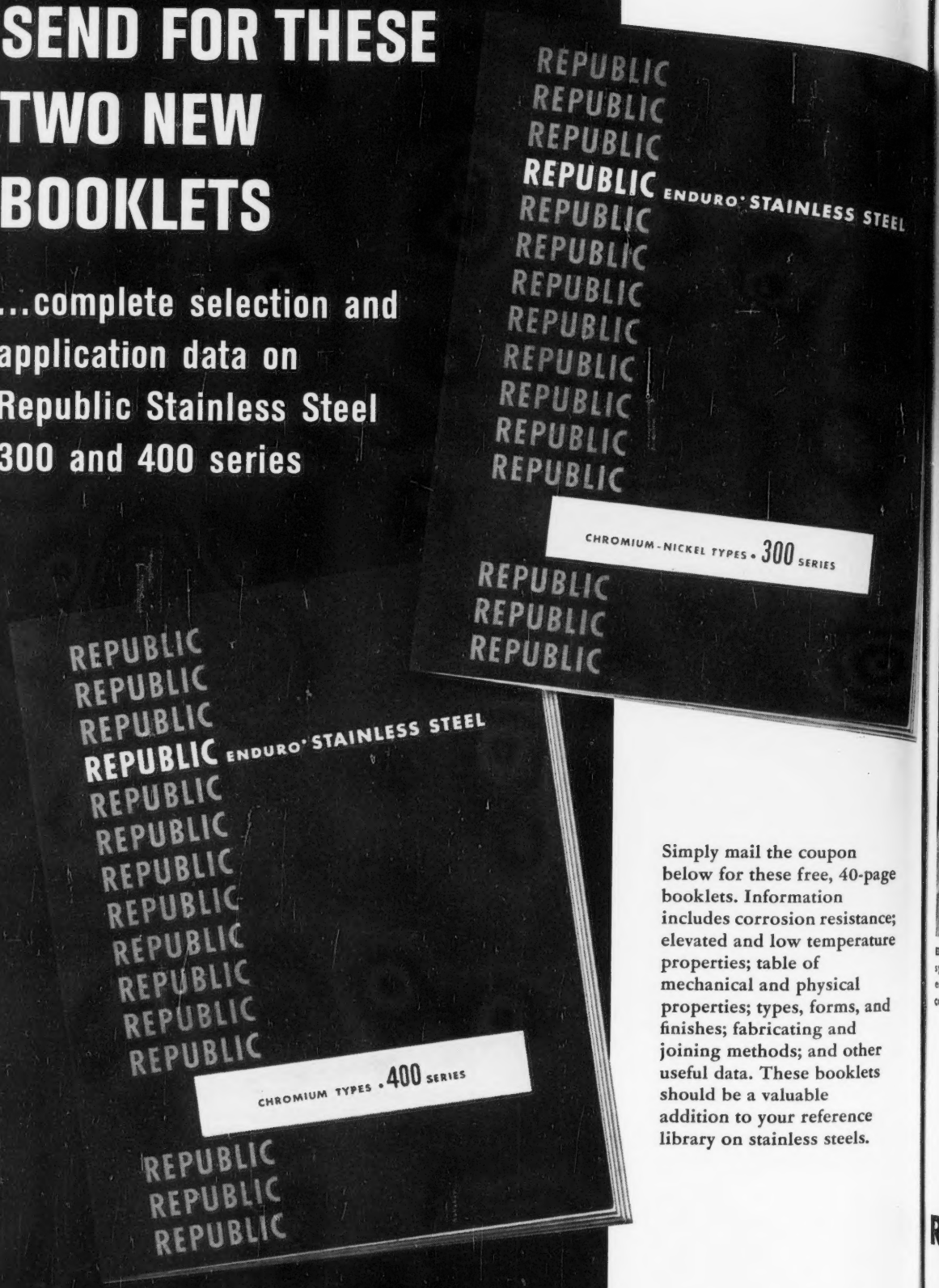

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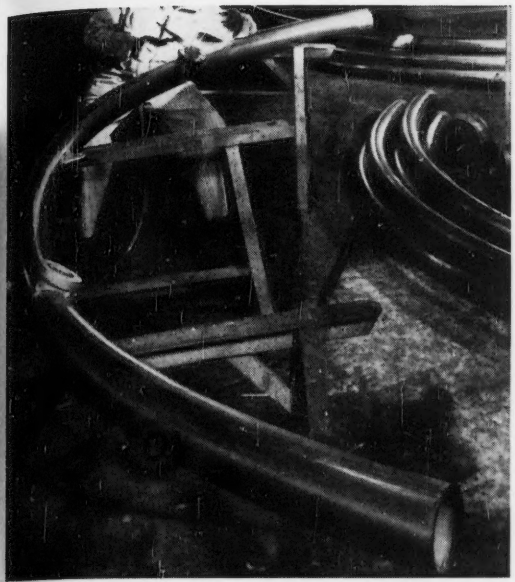

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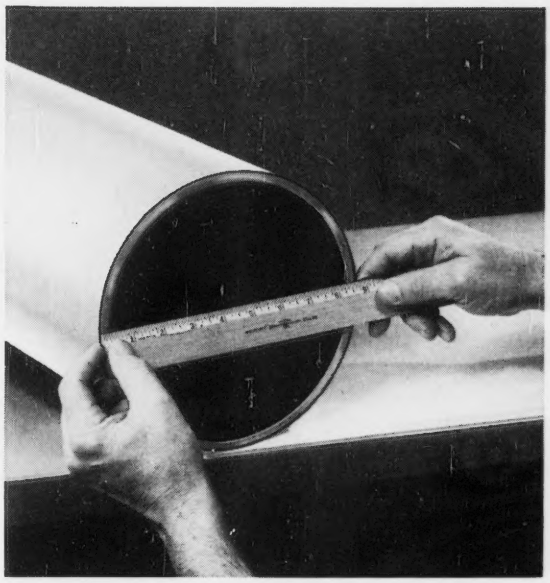

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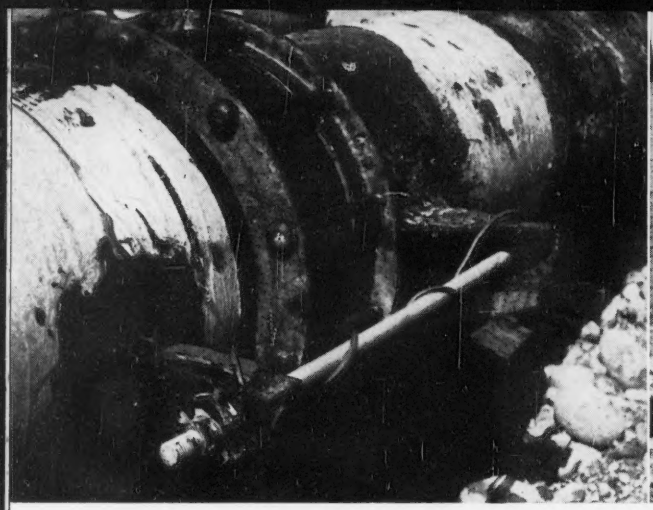

Figure 1—Showing the method of bonding around Dresser couplings on 16-inch water line.

Figure 2—Showing how packaged magnesium anodes were fastened to water line with stainless steel straps.

An Expanding Utility Uses Cathodic Protection*

E. W. Fallis

Public Utilities Commission
Kingston, Ontario, Canada

Abstact

Some of the details and troubles experienced by the Kingston, Ontario Public Utilities Commission in Installing and protecting cathodically its water and gas lines and an elevated water tank are described. Cost data are given on protecting 31,000 feet of gas line. 5.2.1

BEFORE 1955 when the Public Utilities Commission of the City of Kingston, Ontario installed a steel water main under the Cataraqui River, the utility was not especially corrosion conscious. Installation of this 16-inch main, designed to carry 1.5 million gallons of water daily to the Barriefield Army Camp, was made under supervision of consultants who also installed a cathodic protection system. The whole project cost $350,000.

The pipe, coated inside with coal tar enamel, was cleaned, primed and coated outside with coal tar enamel, glass fabric and covered with Kraft paper. Mechanical couplings, tie bolts, nuts and washers were galvanized after fabrication and coated on the job. Flanged joints at each shore end had neoprene-faced insulating gaskets, bolt sleeves and washers. Underwater joints were bonded and 17-lb magnesium anodes were bonded on above water with stainless steel bands.

Strands of No. 4 copper wire were run from a length of pipe near the center of the river to the west shore along with a wire from the first length of pipe on the west shore. At a test point established there, electrical continuity of the pipe could be checked.

★Presented at a meeting of the Canadian Region Eastern Division, National Association of Corrosion Engineers at Toronto, Canada, January 21, 1960, under the title "Introduction of Corrosion Control Methods in an Expanding Utility."

Some Construction Problems

Some of the problems encountered in construction included failure of inside coating in some lengths stored outside over a winter. Also, in order to be sure bond wires were fast it was necessary to give them a strong test pull.

When the packaged 17-lb 4-inch D magnesium anodes were installed along with their backfill of two inches of gypsum in a linen bag, it was learned that wetting them helped compact the package. Thus the bands would squeeze closer to the magnesium core and keep them from falling to the side when the pipe was installed.

A crucible designed for 2/0 wire made a better bond for thermite welding of the 1/0 wire.

After installation in October 31, 1956 potential readings between the pipe and a copper sulfate half-cell showed —1.2 to —1.3 v. In November 1958 potentials had dropped to —1.10 to —1.20 volts, the drop attributed to a change in the resistivity of the coating.

Steel coupons installed in November 1958, one protected and the other not, were checked in April 1959. The protected coupon was covered with a calcareous coating and the unprotected one was rusty and slightly pitted.

Elevated Tank Protected

Twelve ⅞-inch by 22-foot, sixteen ⅞-inch by 4-foot bowl anodes and one ¾-inch by 75-foot aluminum riser anodes were used to protect a 750,000 gallon elevated steel water tank. External power from a rectifier supplying 10.8 to 11.8 amperes was applied to the bowl anodes and 1.9 to 2.2 amperes to the riser anode. The anodes, which need replacing every two years, are removed in the fall and replaced in the spring to avoid ice damage.

Gas Mains Are Extended

In the fall of 1957 an 8-inch steel gas main was installed from the gas plant to a regulator station at Montreal and Rideau streets and then on to a bakery. Soil resistivity in the area traversed was 2000-2500 ohm/cm. Checks the following spring showed potentials between 1.1 to 1.2 volts on the line. When checked in November 1958 a low reading at a regulator pit led to the discovery that insulation in two flange bolts had failed. When repaired, potentials went back to normal.

When natural gas was made available in the spring of 1958 a 5½ mile 8-inch steel main was laid to bring the gas to

(Continued on Page 22)

TABLE 1—Economic Data on Protecting Gas Line

ITEM	Third Avenue[1]	Take Line[2]
Size	8 Inch	8 Inch
Length	4,000 feet	27,000 feet
Cost of test points, insulating gaskets, magnesium anodes, etc.	$ 564.00	$ 1,938.00
Contractors price to install the above	$ 326.00	$ 500.00
Supply and install joint coating	$ 700.00	$ 3,039.00
Pipe coating	$ 1,680.00	$ 11,340.00
Engineering fees	$ 175.00	$ 250.00
Total	$ 3,445.00	$ 17,067.00
Total cost	$52,065.00	$229,234.00
Pipeline cost/ft.	$ 13.00	$ 8.50
Coating & cathodic protection cost/ft.	$ 0.86	$ 0.63
Cathodic protection cost/ft.	$ 0.44	$ 0.21
Coating & cathodic protection as % of total cost of pipeline	6.6 %	7.4 %
Cathodic protection as % of total cost of pipeline	3.4 %	3.4 %

[1] Located under a city street.
[2] Located in fields outside settled area.

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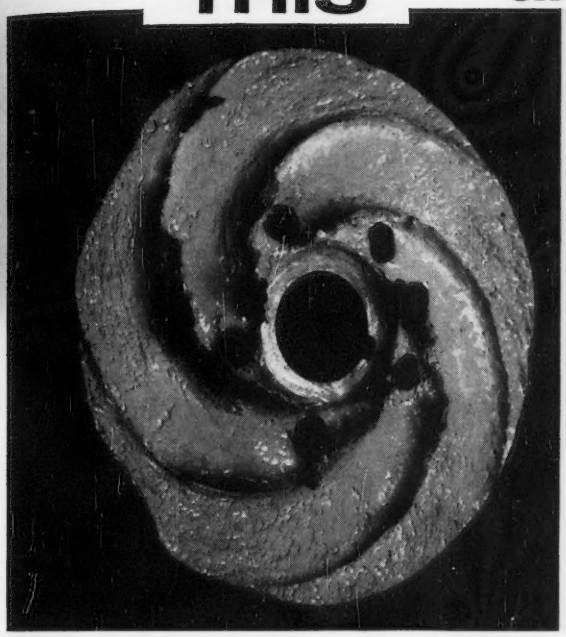

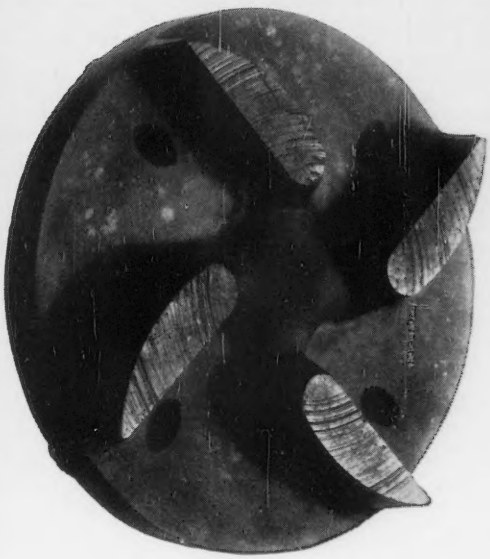

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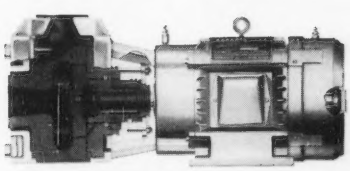
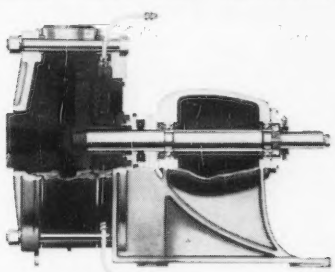


TYPE F MOTOR-MOUNTED "KARBATE" CENTRIFUGAL PUMP
Cross-section illustrates typical "Karbate" motor-mounted pump recommended for heads to 70 feet — capacities to 140 gpm.



TYPE C FRAME-MOUNTED "KARBATE" CENTRIFUGAL PUMP
Cross-section shows typical "Karbate" frame-mounted pump recommended for heads to 120 feet — capacities to 1500 gpm.

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Water Turbulence Increases Galvanic Cell Corrosion★

INTERNAL CORROSION of steel pipes installed in a synchronous condenser cooling system resulted in rapid penetration and failure in certain locations at a large electric substation on the west shore of South San Francisco Bay a few years ago.

Visual inspection of the failed nipples lead operating personnel to believe that erosion caused the trouble. These 2.5 and 1.0-inch ID pipe nipples failed on the downstream side and adjacent to control valves regulating waters flow. Although these restricted areas have turbulent action and increased velocity which accelerate the rate of failure, they were not the primary reasons for failure.

Water for cooling the two synchronous condensers comes from a station well at 175 gallons per minute for each condenser. In this once-through cooling system, water temperature rise is about 7 F in passing directly through the heat exchanger before discharge into the bay. Resistivity of the water was 380 ohm-cm with a NaCl content of 950 ppm. There were no solid particles suspended in the water.

Control valves on the inlet and discharge lines of the main heat exchangers have cast iron bodies and bronze gates. Flow meters, unions and temperature sensing elements also have bronze components.

Inspection of the pipe nipples revealed a loss of metal adjacent to these copper alloy components. No adhering corrosion deposits were found on about 40 percent of the internal pipe circumference on the downstream side nor within three to four inches of the throttling valves and flow meters. All other upstream nipples screwed into fittings containing copper alloy appeared to be coated with tightly adhering corrosion products.

Current flow measurements were made on short sections of pipe screwed into the valves. Current flow on the downstream side was greater than on the upstream side, explaining the metal loss in the affected areas. No current flow was noted on pipe sections adjacent to a fully opened valve in which the bronze gate was recessed into a separate chamber. When the valve was partially closed, current flow began but only after several minutes. This delayed reaction was probably due to the bronze gate being coated with deposits where not scoured by the water stream. When the gate entered the stream, water removed deposits sufficiently to allow a measurable current to flow in the galvanic cell.

These tests showed that the galvanic cells established by dissimilar metals in the water were a major cause of corrosion failures. Deposits on the anodic surfaces normally of higher resistance than bare metal tended to lower the corrosion rate. However, where these deposits were removed by water impingment on the downstream sides of restrictive fittings containing copper alloy, the corrosion reaction continued.

This condition has been corrected by substitution of plastic nipples where destructive corrosion reactions occurred.

★ Extracted from a paper titled "A Miscellany of Mitigated Corrosion Problems of a Public Utility" by H. H. De Laneux and H. A. Medlock, Pacific Gas and Electric Co., Emeryville, Cal., presented at the Western Region Conference, National Association of Corrosion Engineers, September 29-October 1, 1959, Bakersfield, Cal.

Insulation Halts Corrosion On Aluminum Covers★

WHEN ALUMINUM covers were installed on cast iron junction boxes in manholes subject to flooding for considerable periods, a severe loss of metal occurred in the covers. Some needed replacement after only 10 months' service.

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★ Extracted from a paper titled "A Miscellany of Mitigated Corrosion Problems of a Public Utility" by H. H. De Laneux and H. A. Medlock, Pacific Gas and Electric Co., Emeryville, Cal., presented at the Western Region Conference, National Association of Corrosion Engineers, September 29-October 1, 1959, Bakersfield, Cal.

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Cathodic Protection–

(Continued From Page 20)

Kingston. This main was protected cathodically. The 4000-foot 8-inch and 1200-foot 3-inch lines were laid to serve the aluminum company. Cost data on these lines will be found in Table 1.

Eventually the steel mains laid around the city will form a high pressure loop.

Problems Are Encountered

Principal difficulties with the protection systems included, failure of insulation around bolts, an accidental contact between the line and a water main and one accidental perforation of a live gas line. This latter occurred when a 2/0 crucible was used with a No. 115 thermite cartridge to weld a No. 12 wire to a 8-inch line. The charge burned a hole through the pipe.

The utility plans to continue protecting gas mains and extensions, and also to protect a 30-inch water intake pipe with twenty-five 12 x 1½-inch high silicon cast iron segments joined to a special No. 8 cable. The anodes will be installed parallel to the line about 54 feet away at the bottom of the lake. This type of installation was selected because of its long life and weight.

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•

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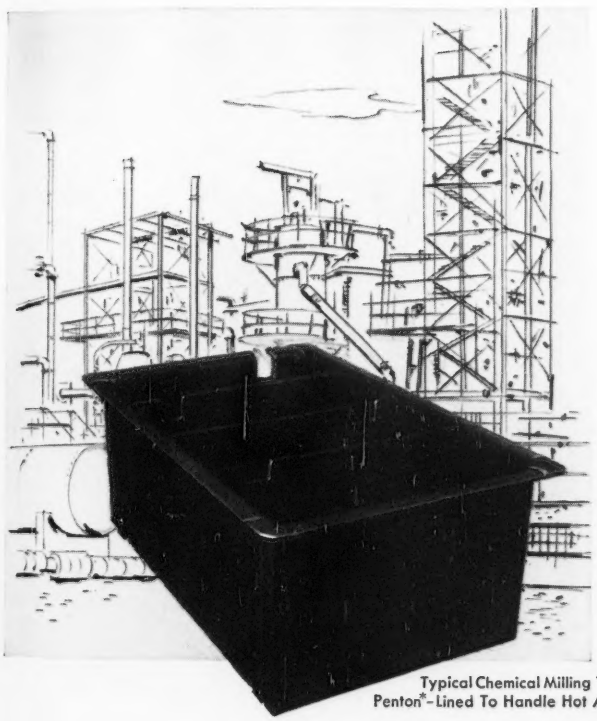

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*Registered Trademark, Hercules Powder Company
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Accelerated Corrosion Tests of Sandwich-Type Construction*

J. E. Halkias
Convair
Fort Worth, Texas

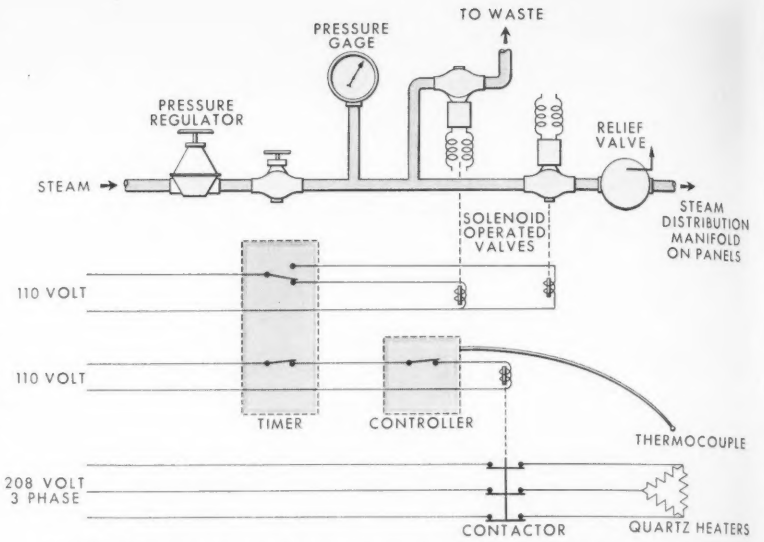

Figure 3—Schematic diagram of alternate wetting and heating accelerated corrosion jig.

Introduction

HONEYCOMB SANDWICH type construction is finding wide application in the airframe industry. This construction provides the increased structural strength and rigidity needed for modern high performance aircraft without great weight. Convair has been a pioneer in the development and use of honeycomb sandwich panels including those in the supersonic B-58 Hustler which fall into two categories: (1) Panels in which the skins are bonded to the core material with adhesives, and (2) those in which the skins and core are brazed to each other with some suitable alloy.

Early phases of the test program on honeycomb structures quickly revealed that several problems must be solved to obtain useable information from corrosion tests normally used by industry to screen materials. In general the tests involved determining mechanical properties of structural materials before and after exposure to accelerated corrosion.

*Revision of a paper titled "Problems Arising in Corrosion Tests for Sandwich Type Construction" presented at a meeting of the Missile Industry Symposium, 16th Annual Conference, National Association of Corrosion Engineers, March 14-18, 1960, Dallas, Texas.

Primary corrosion media used at Convair Fort Worth Division are 20 percent salt spray environment and various relative humidity - temperature environments in which results are dependent upon the media coming into intimate contact with the materials being evaluated.

Some of the first honeycomb sandwich panels exposed to salt spray and humidity environments were cut into smaller test panels and given mechanical strength tests. Although a number were visibly attacked around the edges the mechanical tests on small panels cut from larger panels indicated that the corrosive media had no effect on the construction. Exposed test panels exhibited as much strength as unexposed control panels.

Table 1 contains destructive test data from a random selection of sandwich panels which were fabricated of identical materials and in a common configuration. Each value shown in the table except panel column compression and P/△ represents an average of a number of specimens cut from the large panels. Panels No. 1 through 4 were among the group of large panels which exhibited visible corrosion along the outer edges, but the test data show the panels to be structurally sound.

The first problem was to determine why the data failed to correlate with visual observations made during exposure. This was explained almost immediately. Figure 1 shows typical configuration of welded node honeycomb core material. Each ribbon has perforations along its entire length. When the nodes are welded together, each wall of the individual cells has at least one tiny hole in it necessary to allow volatiles to escape when skins and core are bonded together under pressure and temperature. The holes also allow passage of inert gases into the interior of the cells at the elevated temperatures required during brazing operations. Figure 2 shows an exploded view of a segment of a sandwich panel. When the two skins are brazed or bonded to the core material the only way that corrosives media can enter into the panel interior is through the tiny perforations in the core. Because each cell contained air, salt spray and humidity environments could not penetrate to the inside

(Continued on Page 26)

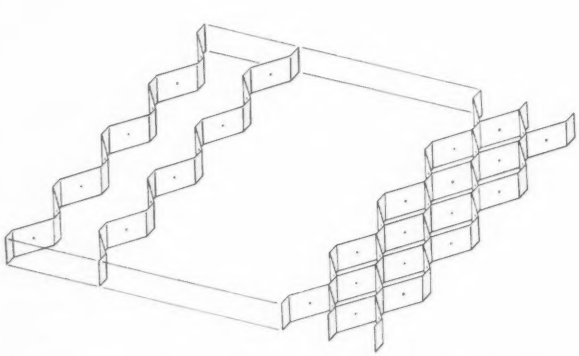

Figure 1—Typical welded node core configuration. Note perforations in ribbons.

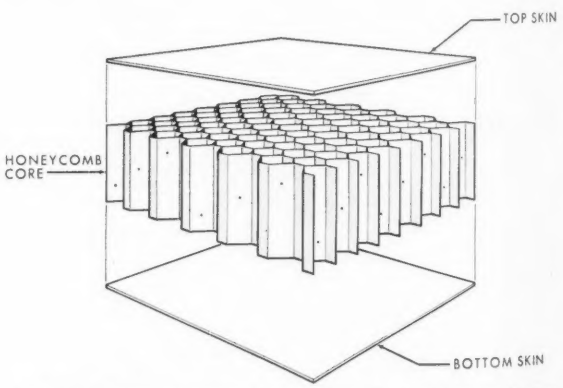

Figure 2—Honeycomb sandwich construction. Top and bottom skins are brazed or bonded to core material. Access of corrosive medium to panel interior is gained only through the perforations.

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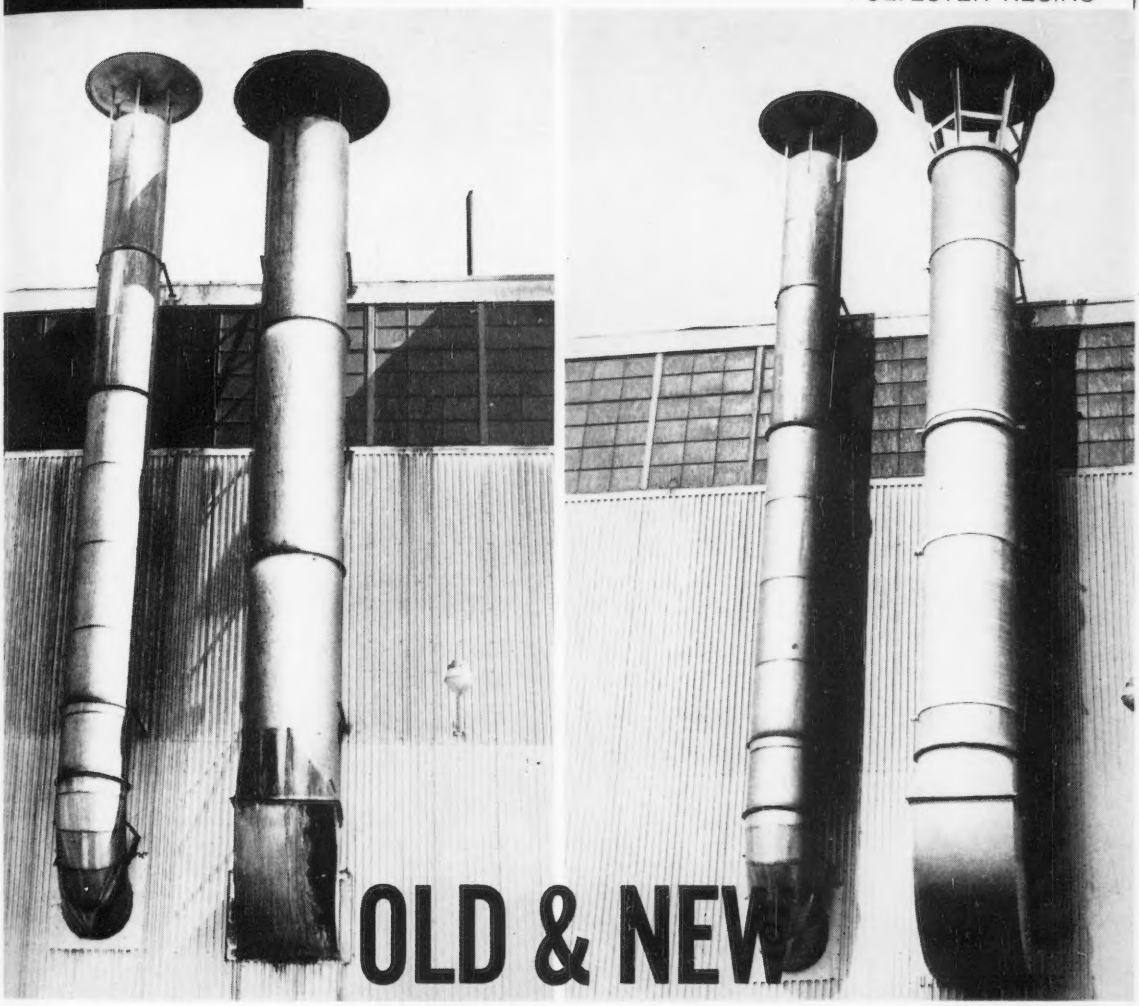

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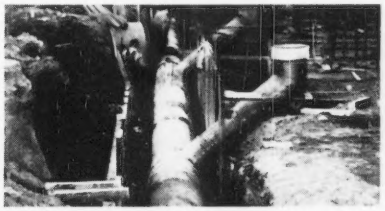

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TABLE 1—Summary of Destructive Test Results on Specimens

Cut From Large Sandwich Panels After Exposure to Salt Spray and Humidity Environments

TYPE OF TEST			No Exposure	50-Hour Exposure To 20% Salt Spray		30-Day Exposure To 120 F, 95% Relative Humidity	
			Control	Panel 1	Panel 2	Panel 3	Panel 4
Tensile Yield, psi			197,650	201,975	201,250	196,409	185,509
Tensile Ultimate, psi			207,700	218,125	209,750	200,587	191,738
Tensile Elongation, percent			2.0	1.75	2.37	2.75	3.8
P/△ Lb./Inch	Specimen No. 1	4″ Span	33,600	34,800	39,300	13,950	28,750
		3″ Span	33,900	35,000	38,250	60,000	46,200
	Specimen No. 2	4″ Span	39,300	37,500	34,900	25,000	18,750
		3″ Span	43,800	40,000	36,150	58,400	50,000
Simple Beam, Ultimate, lb.			965	970	975	885	825
Flatwise Compression, Ult., psi			800	977	945	1,007	1,092
3″ x 3″ Core Shear, Ult., lb.			1,551	1,438	1,860	1,336	1,618
Panel Column Compression, Ult., ksi			151.818	152.000	160.909	139.272	135.454
2″ x 3″ Column Compression, Ult., ksi			173.6	164.2	170.7	156.1	146.5

Accelerated Corrosion—

(Continued From Page 24)

of the panels. So these media attacked only the first few cells along the edges of the panels while the interior sections were unaffected.

Early Attempts to Modify Exposure Method

The next step was to alter the existing or develop new exposure methods which could be used to provide meaningful data. Generally it is easier to alter an existing test procedure to meet new requirements than it is to develop a new one.

The salt spray chamber was modified by including an externally mounted vacuum pump, moisture and salt traps, and plastic tubing which entered the chamber through an opening cut in the top. The tubing was connected to a manifold which surrounded three of the four sides of each panel to be tested. The fourth side of each panel remained open and served as the salt spray inlet.

At the completion of a given exposure period the panels were removed from the chamber and flash heat tested to determine if the exposure could be continued. The flash heat test is the rapid heating of a given area in two to four seconds. This test shows the existence of a poorly brazed area or one weakened by corrosion. Panels are subjected to this test before use, and a flash heat failure after exposure to corrosive media can be used to indicate deterioration of the panel.

Although the vacuum pump arrangement drew salt spray into the cells of the panels, several problems plagued the set-up so operation was not smooth and efficient. The suction line was easily clogged by salt caking at the manifold connections. The salt also caked within certain cells. This caused a nonuniform exposure of the panels. Added to this was the inconvenience of maintaining the moisture and salt traps which protected the vacuum pump.

Table 2 shows the results of several of the "Vacuum applied salt spray exposure-flash heat" tests on various sandwich panels. (Reference to specific panel configurations, braze alloys and other information is omitted.)

Although the vacuum pump modifications could easily be applied to the humidity chamber with probable success Convair was more interested in tests which accelerated corrosion on steel assemblies faster than the humidity-temperature cycle alone is capable of doing. So a decision was made to use a test whereby panels were immersed in water containing a known amount of reagent grade sodium chloride as the corrosive medium.

In an attempt to expose only one skin and the brazed fillets of a given specimen, the panels were laid horizontally in shallow, non-metallic containers, and the

(Continued on Page 28)

Abstract

Procedures for accelerated testing of brazed, honeycomb sandwich-type construction used in high performance aircraft are described. Cyclic tests involving alternate wetting and heating are described, including solution of the problem of introducing corrosives into the structure. Tests described involve segments of full-sized honeycomb panels, and the evaluation of components, some from and others not from full-size panels.

Data derived are useful to discriminate among alternate materials and processes but do not give results necessarily correlated with service experience. Long-time weather and service tests underway ultimately will be compared to accelerated tests to determine if there is correlation. 2.3.2

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TABLE 2—Results of Flash Heat Tests on 17-7 Cres Steel Panels After Vacuum Applied Salt Spray Exposure

Configuration And Panel No.	Type of Braze Alloy	Type of Inhibitor Used	Hours of Vacuum Applied Salt Spray Prior To Flash Heat Failure	Remarks
No. 1 of Type A	Silver Base Alloy "X"	None	96	Control Panel.
No. 2 of Type A	Silver Base Alloy "X"	None	72	Control Panel.
No. 3 of Type A	Silver Base Alloy "X"	2% Sodium Chromate	72	No improvement over uninhibited control panels.
No. 4 of Type A	Silver Base Alloy "X"	2% Sodium Chromate	168	Sectioned panel contained cells plugged with salt. Exposure not uniform.
No. 1 of Type B	Silver Base Alloy "Y"	None	No failure after 192 hours exposure.	Test discontinued due to non-uniform exposure (plugged cells).
No. 1 of Type C	Silver Base Alloy "Y"	2% Sodium Chromate	No failure after 168 hours exposure.	Test discontinued due to non-uniform exposure (plugged cells).

Accelerated Corrosion–

(Continued From Page 26)

salt solution level was maintained so that only half of each panel was exposed. The horizontal immersions proved to be unsuitable because air was entrapped in the cells of the panel. The solution would not enter the cells even when panels were fully immersed.

Vertical Immersion in Salt Water

This difficulty was overcome by immersing the panels vertically in the salt solution. As the corrosive medium rose into the panels it forced the air out through the small openings in the core ribbons. Air entrapment was eliminated and the panels were uniformly exposed to the salt water solution. The immersion test alone gave a good qualitative picture of the corrosion resistance of sandwich panel interiors. It was also flexible in that the effect of corrosion inhibitors could be studied merely by the addition of the inhibitor to the salt solution.

A quantitative measure of the effect of corrosion on the panels could be obtained by conducting mechanical property tests on small specimens cut out of panels given immersion tests and comparing results with those from panels not exposed to the salt solution.

Alternate Wetting and Heating Test

To simulate service conditions to which sandwich panels might be subjected, an alternate wetting and heating accelerated corrosion jig was designed and used on several panels. A schematic diagram of the fixture is shown in Figure 3. Essentially, the fixture consists of a regulated steam source and a heater bank. Timing mechanisms are used to admit steam (at a low pressure) into three sides of a manifolded sandwich panel for a given interval, to cut off the steam flow and bring the panel to an elevated temperature for a given interval, and finally allow the panel to cool to ambient temperature. Low pressure steam is used to introduce moisture within the panel, simulating condensation in panels during flight. The elevated temperature simulates temperatures to which various panels on the B-58 Hustler might be subjected.

At the completion of a given number of alternate wetting-heating-cooling cycles, the panels are flash heat tested to

(Continued on Page 30)

TABLE 3—Results of Flash Heat Tests on Steel Sandwich Panels After Exposure to Alternate Wetting-Heating-Cooling Environment

	TOTAL NUMBER OF FLASH HEAT FAILURES			
	Panel A, Braze Alloy "X"		Panel C, Braze Alloy "Z"	
Total 24-Hour Cycles	Test Specimen	Control* Specimen	Test Specimen	Control* Specimen
0	0	1	0	0
25	1	1	0	0
50	2	1	0	0
75	5	1	0	0
100	Removed from test	1	0	0
125	..	1	0	0
150	..	1	0	0
175	..	3	0	0
200	..	Removed from test	0	0
225	..	..	0	0
250	..	..	0	0
275	..	..	0	0
300	..	..	0	0

* Control specimens received no heating cycle.
Note: Panels are considered a loss after three flash heat failures.

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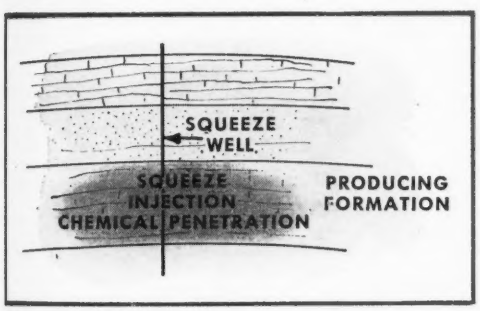
Visco has found squeeze treating of sufficient interest to producers to justify development of specialized chemicals and techniques to permit most effective use of the method.



Squeeze technique forces chemical corrosion inhibitor into formation around well bottom. Chemical is carried back with produced fluid. The excellent film persistency of Visco squeeze treating chemicals assures long-lasting, low-cost well protection.

Effects of Formation

Producing formation composition, porosity permeability and position can have an important bearing on the success of squeeze treatment corrosion control . . . They are important considerations in the development of special Visco formulas for this purpose.

Determining Chemical Type

As with any operation affecting producing formations, experience is the most dependable guide. Chances are great that the conditions you have in your area have been closely paralleled by other Visco squeeze treating experience. Further, Visco Formulas such as

Visco's J. P. Stanton, Product Manager for Corrosion Control Chemicals, discusses factors considered important in assuring effective squeeze treatment.

S-1390X, 956, S-1339X, were developed to broaden the effectiveness of corrosion control with squeeze treatment, and so are a big help in pinpointing the best chemical and method to apply to specific well characteristics.

Field Experience

Squeeze treating can offer some substantial cost and time advantages for effective corrosion control in many types of producing wells . . . BUT, probably more than any other treating method, squeeze treatment demands skill and experience, as well as effective chemicals, to assure success. No one is better equipped than Visco . . . *we* firmly believe no one else can do as well for you.

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FOCUS ON PLASTICS in PROCESS EQUIPMENT

Five interesting discussions of of plastic applications for process equipment will be published in the Technical Topics Section of the November issue of CORROSION.

Accelerated Corrosion—

(Continued From Page 28)

determine if the test should continue. Table 3 lists results of this type of test on two sandwich panels which differ only in the type of braze alloy used in fabrication.

The test has several advantages. No air remains inside the panel during the wetting cycle and they are uniformly exposed to moisture. The test simulates actual service conditions with one exception: It does not take into account vibrational conditions which might be encountered in flight. Convair chemists presently are considering modification of the jig to include a vibration cycle. The flash heat test is a rapid qualitative test for corrosion after exposure. The effect of corrosion also can be given a quantitative value by following up the exposure cycle with physical tests.

Changing of Test Specimen Configuration

Previously mentioned tests involve using entire sandwich panels for exposure purposes. The cost of such panels is extremely high. However, very useful information can be obtained from smaller specimens of the same material combinations under investigation.

Immersion, salt spray and humidity tests may be used on smaller specimens to screen obviously bad combinations of skin, core and braze alloy. A typical specimen can be made by brazing small pieces of core to pieces of skin. Another specimen configuration which Convair has used successfully is shown in Figure 4. It consists of a small metal cap brazed to a metal coupon and is used in conjunction with immersion tests. It is removed from the corrosive medium daily and flexed over a semicircular mandrel. The cycle is repeated until the specimen cap pops off or until a given time has elapsed.

The advantages of this specimen configuration are threefold: It is easily constructed, cheap, and gives a good indication of the nature of the attack, whether it be galvanic, pitting, contact or other type of corrosion.

Another small specimen configuration which lends itself to immersion tests is shown in Figure 5. It is called the flatwise or "π tension" test specimen. The name "π tension" comes from the fact that the test area of the specimen is numerically equal to π square inches. Since the π tension specimen is cut from an actual test panel, it is more expensive to fabricate than the flexure specimen shown previously. However, it has one advantage in that the specimen can be loaded in tension after immersion, thereby giving physical data which indicates the structural worth of the material combinations after exposure to corrosion environment.

TABLE 4—Results of Tensile Tests on π, Tension Specimens After 6 Days' Immersion in Inhibited and Uninhibited 1% Salt Solutions

Control Specimens (No Exposure)	Specimens In 1% Sodium Chloride Solution With 2% Sodium Chromate Inhibitor	Specimens In 1% Sodium Chloride Solution With No Inhibitor
Ult. Load At Failure, psi	Ult. Load At Failure, psi	Ult. Load At Failure, psi
1911	1225	690
1975	1160	925
2060	1425	740
	1390	535
	890	600
	1338	790
	1210	815
	1140	860
	1389	713
	1045	873
	1325	720
	1293	522
Avg. 1983	Avg. 1236	Avg. 732

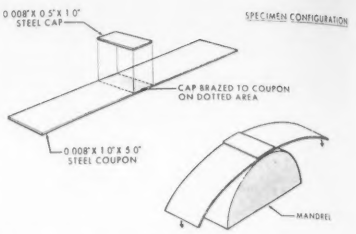


Figure 4—Immersion specimen in flexural bend test.

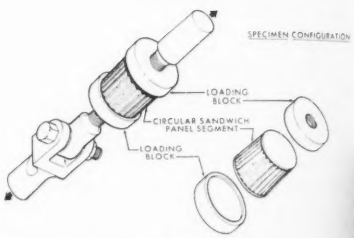


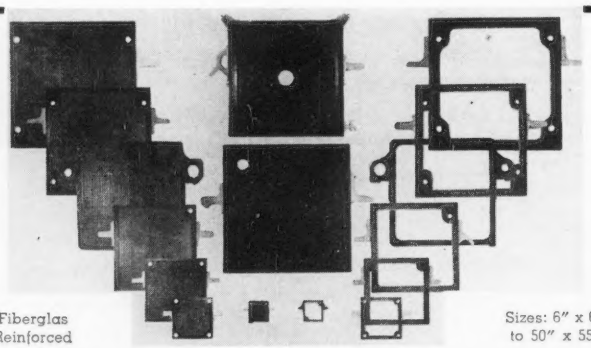
Figure 5—Specimen configuration for flatwise tension test.

Some typical tensile test results obtained from π tension specimens after immersion in salt water solutions are given in Table 4. Note that some of the individual tensile values vary from 200 to 300 psi from the average values. Such a spread in data must be expected when conducting physical tests on materials having a cell type configuration and extremely thin wall thickness. Therefore, a large number of specimens are generally required to determine what effect various corrosive environments have upon the physical strength of honeycomb sandwich type construction.

Brighter Outlook for Future Test Programs

In summation it should be pointed out that sandwich type construction has many advantages which will increase its use. It is well known to the corrosion engineer that modification of an existing test procedure or the development of a new type of test does not in itself tell the entire corrosion story. Results from these tests make possible comparisons between one set of materials and another in a given environment. But this tells little concerning how long a given material combination will last under actual service conditions.

Convair Fort Worth's test program on sandwich panels continues. Weather exposure test programs begun several years ago on sandwich panels which looked promising will continue for years to come. Eventually an attempt will be made to correlate accelerated corrosion tests developed for sandwich panels, long range weathering tests, and service life on various airframes.



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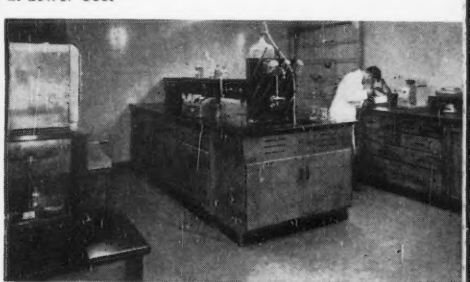

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Mine Waters Cause Grooving Corrosion on Welded Steel Piping*

F. P. A. Robinson

University of the Witwatersrand
Johannesburg, South Africa

Abstract

Describes grooving corrosion attack on welded steel pipe used as pumping columns in South African mines. Outlines metallurgical examinations, chemical analyses, electrochemical studies and residual stress tests made to determine exact cause of the corrosion. Briefly discusses preventive and control measures being used and tested. Photographs, tabular data and graphs. Concludes that grooving corrosion was casued by residual stresses in pipe. 4.6.8

EXPECTED LIFE of welded steel piping used for pumping columns in all mines in South Africa is about 20 years, but severe corrosion has caused pipe failures in many cases after only three years. Some failures occurred in even less time.

The pumping column corrosion took the form of severe grooves and pits as shown in Figures 1 and 2. The grooves were in a narrow zone on both sides of the weld metal and at what appears to be the interface between the weld and parent metal. The pits shown in Figure 2 were about ¼-inch deep.

This corrosion reduced the pipe wall thickness to such an extent that ruptures and leaks occurred because of the hydrodynamic pressure.

This internal corrosion was caused by corrosive waters used which had high contents of chloride and sulfate. Of course, chloride and sulfate can cause severe corrosion under all pH conditions, but under neutral or near neutral conditions found in treated water, these two anions can cause catastrophic pitting. Analyses of the waters used in the mine pumping columns are given in Table 1.

Grooving and pitting corrosion shown in Figures 1 and 2 occurred on welded pipe produced by the submerged arc process. On solid drawn pipe, impingement attack was found on the top inner surface of inclined piping columns. This attack produced a deep longitudinal U-shaped pattern as illustrated in Figure 3.

External corrosion of the piping also occurred. Figure 4 shows this corrosion along the welds which was caused by underground conditions of high humidity and heat, thus producing continuous moisture condensation.

*Revision of a paper titled "Corrosion of Welded Steel Pump Column Piping Handling Acid Mine Waters."

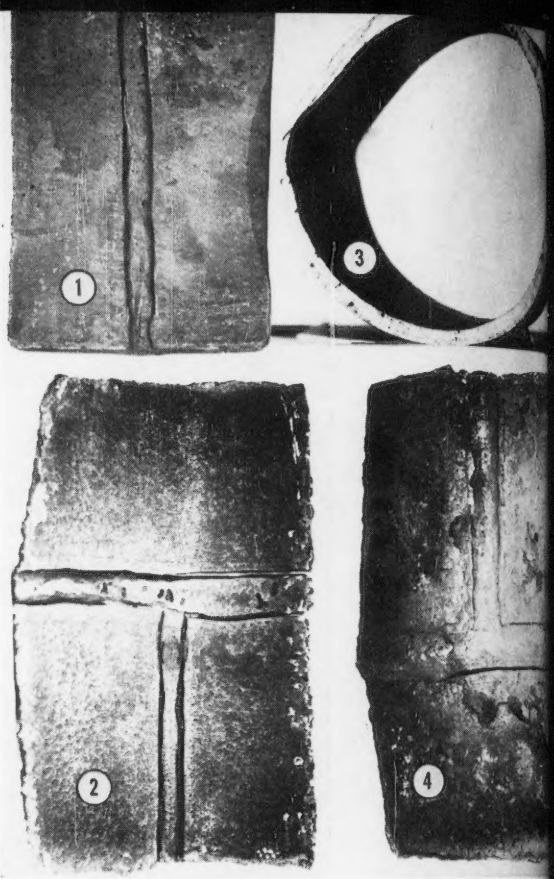


Figure 1—Grooving corrosion attack on welded steel pipe. Figure 2—Pitting of weld metal and grooving corrosion along the longitudinal and circumferential welds. Figure 3—Impingement corrosion produced a U-shaped pattern on this seamless pipe used as an inclined pump column. Figure 4—Welded pipe burst as a resutl of corrosion along the welds. Severe corrosion also occurred on the outer surface of the pipe.

Close examination of the corrosion failures revealed the following factors:

1. Corrosion was most severe at the top sections of the pumping column.

2. Pumping columns in which pumps were operated continuously were most severely corroded.

3. Accelerated corrosion may have been caused by water-hammer vibrations which probably stressed the pipe.

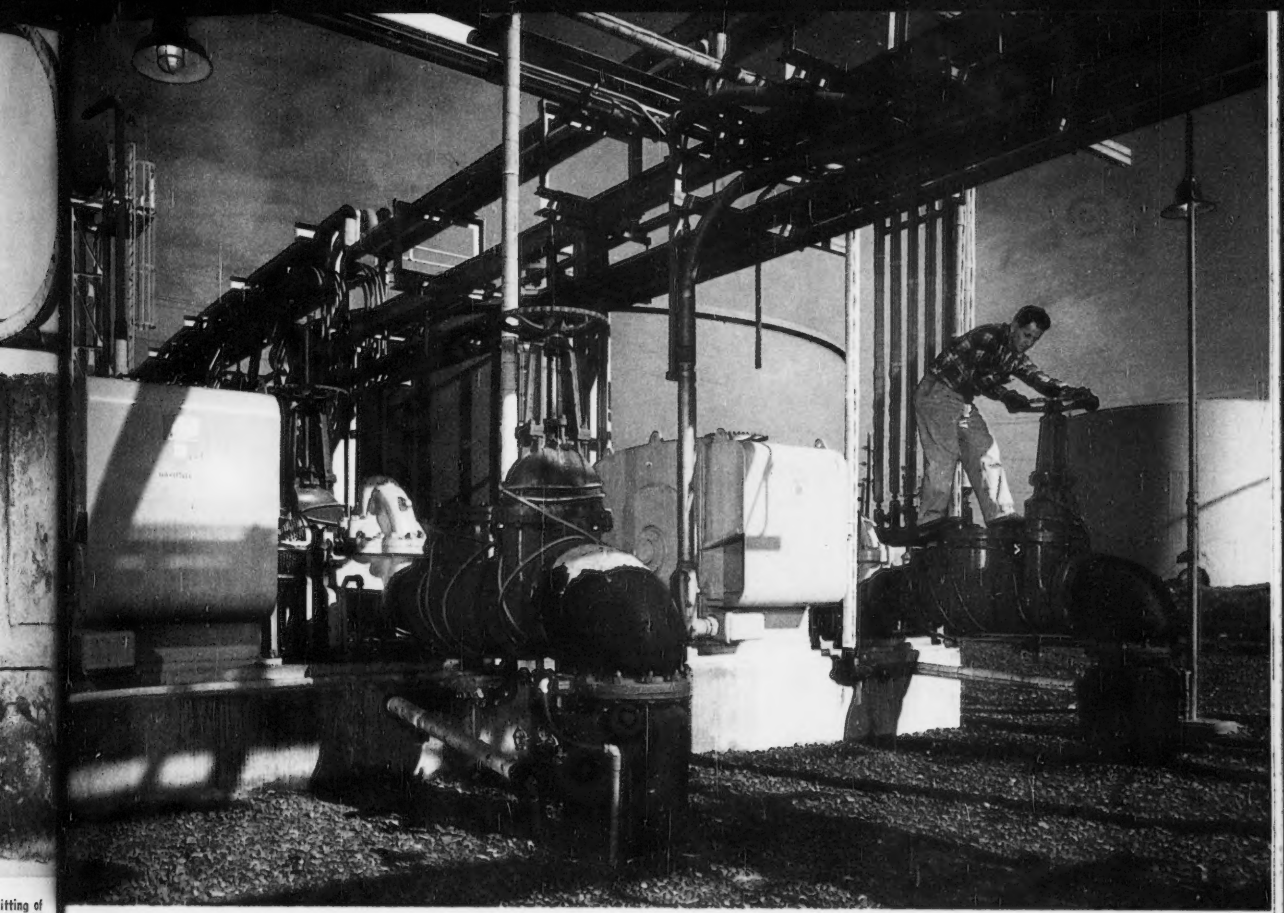
4. Corrosion was more severe in pipes where reciprocating rather than centrifugal pumps were used.

5. Stray currents from underground traction systems can accelerate corrosion by producing electrolytic effects on the external pipe surfaces.

Metallurgical Examinations Made

Because the welded pipes corroded in straight lines parallel to and on both sides of the weld, a purely metallurgical approach was taken first to determine the exact nature of the corrosion problem. Corroded pipe samples were taken from five mines: Robinson Deep, Libanon, City Deep, Consolidated Main Reef and Free State Saaiplaats. Attention was confined to pumping column samples taken near the surface because the corrosive attack had been most severe at that level.

(Continued on Page 33)



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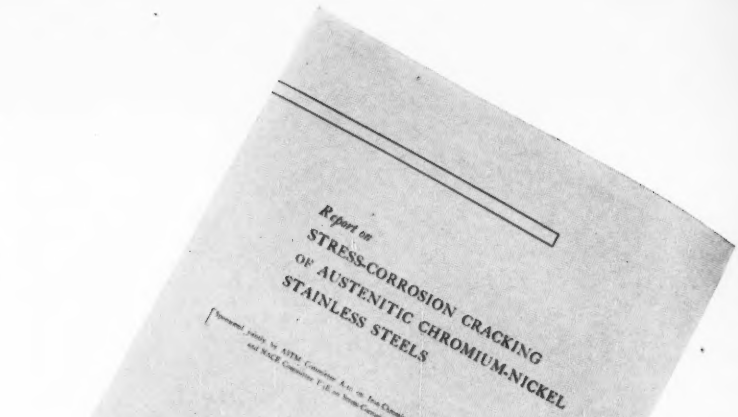

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Grooving Corrosion—

(Continued From Page 32)

After specimens were polished and etched, photomicrographs were made of the significant features (see Figures 5 and 6). The photomicrograph showed grooving corrosion was confined to the overheated zone in the heat affected area. The attack apparently began in the overheated zone, but grooving corrosion did occur to a slight extent in the parent metal (Figure 7A) and the grain refined zone (Figure 7B). The obvious explanation is that this area where the attack began must be anodic to the surrounding steel, which in this case is weld metal and steel away from the heat affected zone. Corrosion was accelerated because of the unfavorable configuration of very small anodes along the line where grooving occurred and the large area of surrounding unaffected material.

Chemical Analyses

Chemical analyses of the pipe samples showed that the metal conformed to Iscor S.S. 10/201 specification for welding quality steel which stipulates the following percentages: 0.18 carbon, 0.4 to 0.6 manganese, 0.05 phosphorus, 0.05 sulfur, and 0.15 silicon.

To determine the source of electrolytic action between the narrow zone on each side and adjacent to the weld (anode) and the surrounding cathodic area, chemical analyses were made to detect chemical composition differences between weld metal and parent metal. Any significant change in composition would affect the adjacent overheated zone by dilution.

The weld metal was sectioned from a Robinson Deep Mine pipe sample. After all traces of parent metal were removed by grinding, the chemical analysis of weld and parent metals (Tables 2 and 3) showed no significant composition difference. The silicon percentage was slightly higher in the weld deposit, tending to make the weld more noble than the parent metal. Only traces of copper were found, probably picked up from the copper backing bar used in welding. These copper traces would tend to set up electrolytic action between the contaminated weld metal as cathode and the parent metal as anode.

TABLE 1—Typical Water Analyses in Parts Per Million

	Libanon	Rob. Deep	St. Helena
H_2SO_4	40	71	65.9
Aluminum	10.7	145	3.2
Calcium	82	506.3	63.8
Chloride	106.4	117	2226.9
Magnesium	27.1	208.4	6.6
Manganese	3.5	61.9	.....
Silicon	12.6	29.0	4.0
Sulfate	572.1	3526.5	.....
Total Dissolved	1132.0	5832.0	4088.0
SOLIDS			
Total solids in suspension	32.3	2080.4	.....
Organic matter	.....	.....	286.3
pH	4.67	4.12	8.2
Alkalinity*	.....	.....	40.0
Temporary Hardness*	.....	.....	40.0
Permanent Hardness*	.....	.....	268.8
Total hardness	.....	.....	308.8

Because only trace differences were found, the electrolytic corrosion obviously was caused by some other agency. This is proved by a pipe sample examined which had such excessive copper pick-up that undissolved copper was visible on the weld's surface in contact with the corrosive water. This sample showed no serious grooving corrosion after seven years' continuous service although it did have some pitting.

Electrochemical Studies

To verify the conclusion that composition differences in the pipe were not the cause of the grooving corrosion, electrode potential measurements were made. Potential values obtained at any given instant were not significantly different for the parent metal, weld metal or overheated structures, thus indicating the absence of electrolytic action between the different phases of the same steel. For electrolytic action to take place, a potential difference of over 100 millivolts would be expected.[1]

Test for Residual Stresses

After electrolytic causes were eliminated by the above tests, studies were made to determine what part residual stresses might play in the severe corrosion on the pumping columns.

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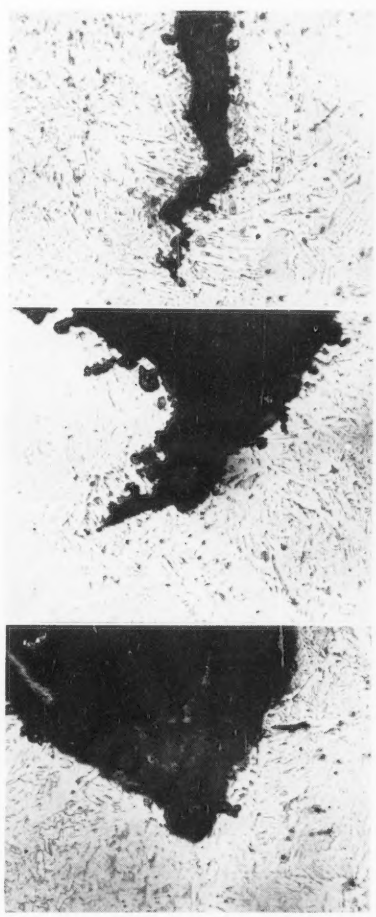
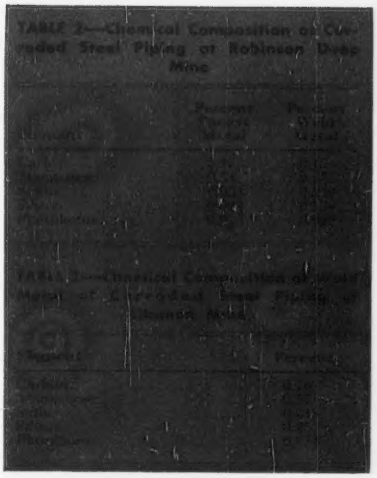


Figure 5—Photomicrographs showing the penetration of grooving corrosion through interface between the overheated zone and weld metal. Etched in 2 percent Nital. 245X.



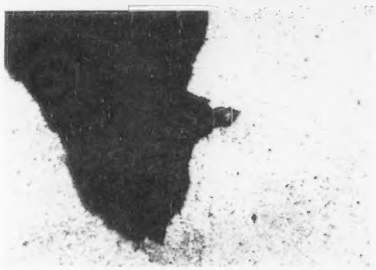


Figure 6—Grooving corrosion penetrated the interface between weld metal and overheated zone in this photomicrograph. The pit branching to the side has penetrated the overheated zone. Etched in 2 percent Nital. 96X.

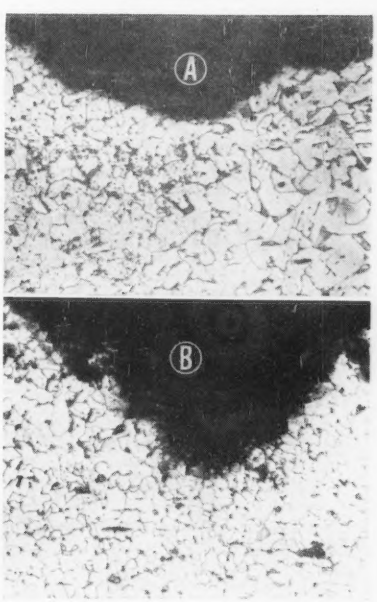


Figure 7—Photomicrograph A shows shallow grooving corrosion in the parent metal; photomicrograph B in the grain refined zone. Etched in 2 percent Nital. Approximately 300X.

Figure 8—Macro-photograph showing V-shaped corrosion pattern of the grooving corrosion. Dotted line illustrates path of hardness trace measurements to determine areas of stress. Approximately full size.

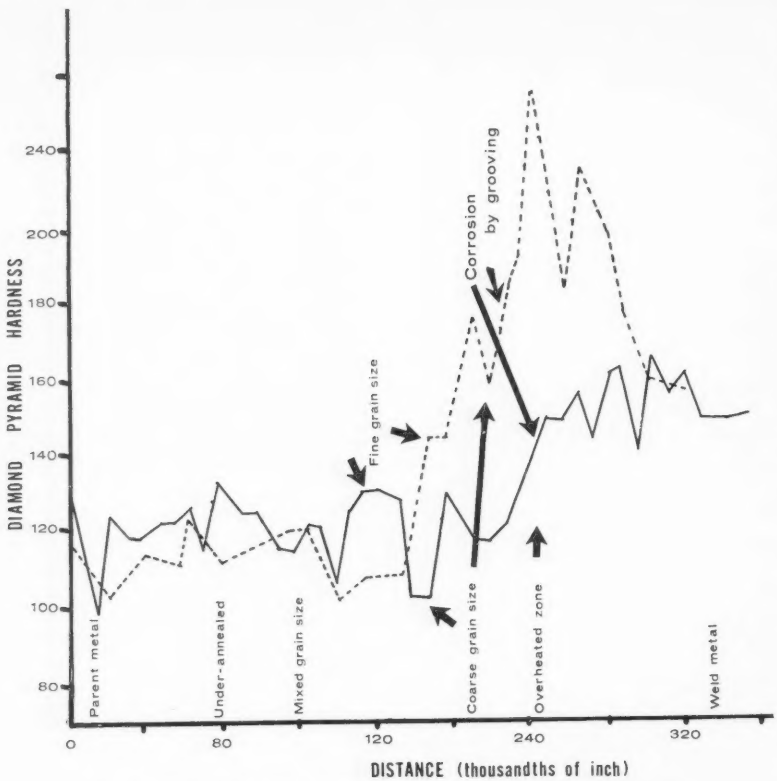


Figure 9—Microhardness traces across welded steel pipe which had corroded in service.

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Those who bind CORROSION by volumes and who customarily extract Technical Section pages are reminded that it will be desirable to extract also the Technical Topics Section and add it to the Technical Section of each issue. Although the Technical Topics Section does not have cumulative numbering of pages, it will be relatively easy to locate articles if this procedure is followed.

Grooving Corrosion—

(Continued From Page 33)

Welded piping contains considerable inherent residual stress because of the production method: bending hot rolled steel plate into a cylindrical shape, tack welding and then seam and circumferential welding. The cold forming stresses alone are strong enough to pull the pipe apart. The pipe tested had a one-inch gap or spring-back when the pipe was sectioned. These tensile stresses are concentrated at the weld interface, which was the focal point of the corrosion.

To determine qualitatively the high stressed regions of the pipe which had undergone slight plastic deformation, a pipe was sectioned transversely to the grooving corrosion and metallographically polished. Hardness traces were made across the specimens at 0.004-inch intervals from the weld into the parent metal. These traverses were made to pass near the tip of the grooving attack (as seen in Figure 8) to detect stressed parts if present.

Results of these hardness traverses (shown graphically in Figure 9) indicated that the interface between weld and parent metal was a high residual stress zone, revealed by sharp inflections in the hardness trace curves. These zones are more reactive (or anodic, in electrochemical terms) to the unstressed steel and therefore are preferentially dissolved out. For this to occur, a potential difference must exist between these areas. To date, existence of such an effect has not been detected experimentally. Further research is being conducted to investigate the influence of stresses in the elastic and plastic range on the corrosion potential of steel.

Once corrosion has begun on the steel pipe, the unfavorable configuration of large cathode area and small anode produce a high corrosion rate. The narrow interface is corroded away until the pipe cross section is reduced so that failure occurs. This failure is a stress acceleration phenomenon—not to be confused with stress corrosion cracking. None of the pumping column failures examined showed any evidence of cracking.

Controlling Grooving Corrosion

All methods of corrosion control and prevention were considered in solving the grooving corrosion on the steel pipe. Economics eliminated several control methods because thousands of feet of a relatively cheap finished product were involved. Economics eliminated the use of a more corrosion resistant alloy such as stainless steel, Monel, silicon-iron, etc. Cathodic protection would be difficult to install for internal protection of long pipe lengths and also would be very expensive.

At present, all mine water is treated with lime to increase the pH. Addition of slaked lime is not as expensive as proprietary inhibitors but is not as effective as anticipated. An inner coating of calcium sulfate forms in the pipe from the water treatment, requiring frequent mechanical cleaning.

A post welding heat-treatment, such as full annealing or stress relieving, should eliminate grooving corrosion and produce a more uniform attack which would probably cause fewer catastrophic failures. But such treatment would not alleviate hydrodynamic stresses from water-hammer and pumping effect. Proper engineering design should, however, ensure that these stresses are within the elastic range.

Suitable protective coatings obviously are the answer to solving this particular corrosion problem. These coatings would have to be non-reactive to acid mine water and be resistant to wear and abrasion from solids suspended in the water.

Galvanized coatings have given some protection[2] but are only temporary because they are dissolved sacrificially.

Vinyl and epoxy resin base coatings have the requisite corrosion resistance but are liable to abrasion damage.

Coatings thicker than 0.010-inch of paints, plastics and metal are being tested to find a satisfactory protective coating for the inside and outside of the pump column piping.

Acknowledgments

The author wishes to thank the University of the Witwatersrand for permission to publish this article and to the management of Hall Longmore & Co., Ltd., without whose sponsorship and cooperation this research would not have been possible.

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1. W. D. Clark. *Metallurgical Reviews*, 3, No. 11, 279-325 (1958).
2. L. W. P. Van Den Bosch. Underground Managers Report from St. Helena Gold Mines, Ltd.

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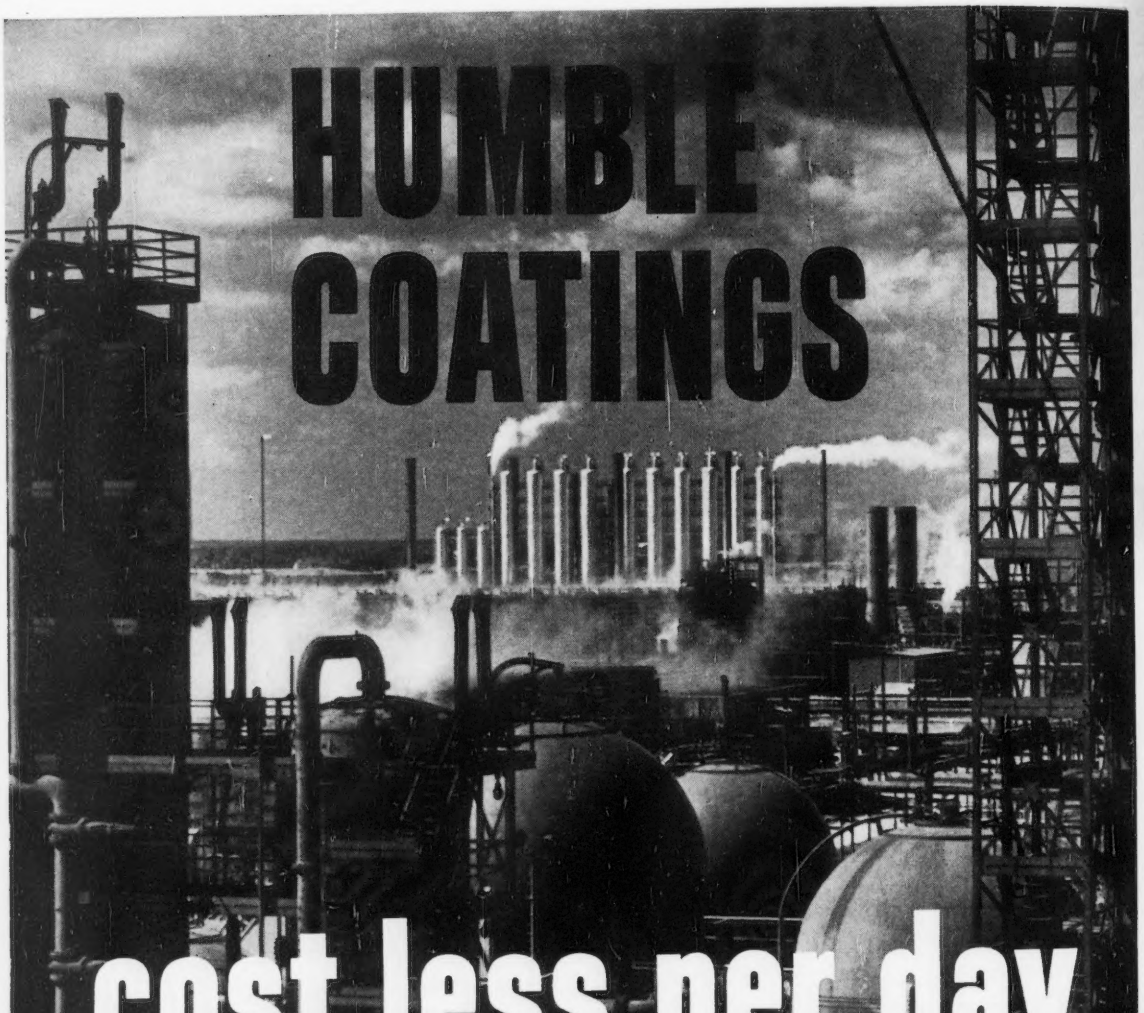

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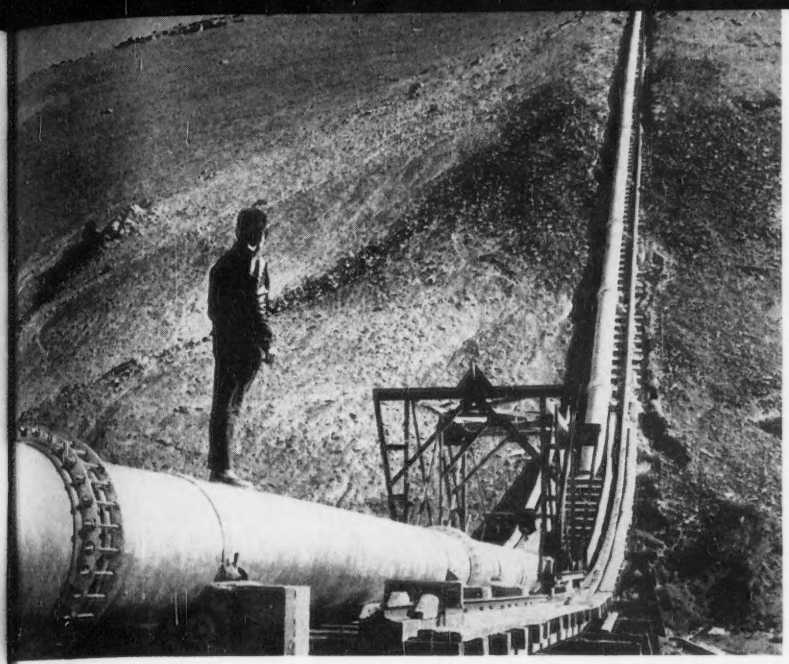

HIGH FLOW RATES for this steel pipe were part of the design considerations when a coal tar lining was applied internally. The pipeline carries process water for a copper mine and ore concentration plant in the Andes Mountains of El Salvador. The lining was designed not only to prevent pitting and corrosion but to maintain a smooth surface inside the pipe for higher flow rates than could be achieved on a long term basis with unlined pipe.

Pipe Lining Used to Control Corrosion, Improve Flow Rates

Coal tar internal lining for steel pipe used to supply process water for a copper mine and ore concentration plant in the Andes Mountains of El Salvador is not only preventing corrosion and pitting but also is maintaining higher flow rates than an unlined pipe of the same diameter.

The 28-inch pipeline, which transports water from a reservoir 20 miles from the plant, handles 28 cfs; the capacity of an unlined 28-inch pipe would be approximately 22 cfs within a relative short time. In terms of power, this means that 3800 kw can be generated instead of 3000 kw.

The coal tar lined pipe supplies the 1½ tons of new water which is needed in addition to the 4½ tons of reclaimed water to concentrate each ton of copper sulfide ore. The pipeline also makes possible an ultimate hydro-electric power generating capacity of 3800 kw, a considerable asset in an area where the delivered cost of steam generated electricity is 1.5 to 1.75 cents per kilowatt.

The lined pipe was designed for a Hazen-Williams roughness coefficient of C=140; unlined pipe would have been about 100. Tests under operating conditions indicate a higher coefficient approaching 150. The lining has been designed to retain its smoothness for many years even when carrying corrosive water.

The lining operation was conducted at Llanta, Chile. Blocks of coal tar enamel were broken up and melted in kettles at temperatures of about 490 F, the temperature considered best for application by spinning.

During the lining, the pipe was rotated continuously to insure a smooth finish and uniform 3/32-inch thickness of the hot lining. Each piece of pipe was inspected electrically for possible defects which were corrected by brushing.

Cooling System Leaks Caused by Rapid Corrosion Damage

Rapid corrosion damage to air conditioning systems in large office buildings in urban areas where the atmosphere is heavily contaminated by sulfur dioxide is demonstrated in a case history of a 1720-ton cooling system in the 35-story McGraw-Hill Building at 330 West 42nd Street, New York City.

Leaks at several points in the building's cooling tower piping gave the first indication to damage only 18 months after the system went into operation.

the smaller units could be placed at

The building is cooled by packaged over a single tower for esthetic reasons: tions on the structure's various setbacks. This complex arrangement was selected through 14 separate cooling tower systems units using cooling water circulated involving 18 towers in six different locavarious places without altering the building's silhouette. Cooling towers are of the forced draft and induced draft type.

The corrosion damage first was suspected to be caused by electrolysis from stray direct currents picked up by the piping system. An analysis of the cooling waters showed a severe acidic condition with pH readings as low as 4.0 in some of the systems. Though no evidence of electrolytic damage was found, a serious slime problem was noted along with foaming in all the induced draft towers. Corrosion was well advanced in all the towers. This was attributed to the SO_2 concentration in the circulating water, picked up as the water is sprayed through the atmosphere.

A thorough cleaning and chemical water treatment program was begun which carried the system through the 1959 cooling season without further incident. The whole installation first was cleaned completely. A slime dosage program was begun, consisting of regular inspections and application of a hypochlorite chemical as required. The cleaning problem was made difficult because of non-removable refrigerant condenser heads in the air conditioning units. Backwash connections were installed to permit periodic flushing of the units.

Chemical treatment of the circulating water was conducted by Water Service Laboratories, 615 West 131st St., New York 27, N. Y. Chromate is fed proportionally into the cooling towers by a device. Technicians analyze water samples at frequent intervals during the season to check on the accuracy of the corrosion control.

Building Research Chairman

NACE Member Woodrow E. Kemp of Koppers Company has been appointed chairman of the Planning Committee on Paints and Coatings of the Building Research Institute.

The Institute's fall conferences are scheduled for November 15-17 at the Shoreham Hotel, Washington, D. C.

UNDERWATER GEAR for fiberglass 10-passenger crew and work boat was fabricated from wrought iron plates and bars. Rubber, bearings housing and accessory equipment were made of wrought iron for resistance to salt water corrosion. Designed for operations out of Galveston, Texas, the 30-foot vessel was built by the Polymer Engineering Corporation, Hitchcock, Texas.

Focus on Plastics in Process Equipment

Applications of plastic materials for process equipment will be discussed in the Technical Topics Section for November.

Abrasion Resistances Checked Faster on Protective Coatings

Increased speed, ease and precision of measuring the abrasion resistance of protective coatings have been made by the National Bureau of Standards. Improvements in the abrasive jet method have resulted from continued studies by A. G. Robert, who originally developed the method in 1955.

In the basic method of measurement, pressurized gas propels an abrasive powder from a vibrating storage chamber through a nozzle onto the test specimen. Abrasive flow, pressure, distance and angle are closely controlled. Abrasion resistant is measured by the time required to abrade through the coating and is expressed in terms of a unit thickness. The first show of bare substrate is the end point and is clearly detected by an abrupt change in color or gloss.

The high speed of the particles in the abrasive jet provides a rapid rate of abrasion that permits most coatings to be tested in a matter of seconds. The abrading conditions can be varied over a wide range to permit the testing of virtually any type of coating.

Studies have shown that the method is not limited to organic coating materials for which it was designed originally. It also is applicable to ceramic, porcelain and anodic coatings as well as films and tapes when attached to a rigid substrate. Sheets of aluminum, brass or steel also can be tested; their rates of abrasion are about the same as those for the more resistant types of organic coatings. A good qualitative correlation has been observed between test results and the service performance of protective coatings applied to military aircraft.

Technical Papers to Be Published in November

Corrosion of Tube Materials by Boiler Sludge, by E. Howells, T. A. McNary and D. E. White

Corrosion Problems in the Use of Salt Solutions as Packer Fluids, by C. M. Hudgins, W. D. Greathouse and J. E. Landers

Some Factors Governing the Corrosion Testing of Zircaloy Base Fuel Alloys, by Stanley Kass and R. F. Gessner

Selective Corrosion of Inconel, by F. Kern and R. Bakish

Stress Corrosion Cracking of High Strength Tubular Goods, by R. S. Ladley

Stress Corrosion Cracking in Concentrated Sodium Nitrate Solutions, by R. L. McGlasson, W. D. Greathouse and C. M. Hudgins

High Temperature Furnace Corrosion, by R. D. Merrick

Cracking of Low Carbon Steel by Ferric Chloride Solutions, by Mary Boehm Strauss and M. C. Bloom

Things New or Unusual in Mitigation of Corrosion in the Utilities Field, by E. H. Thalmann

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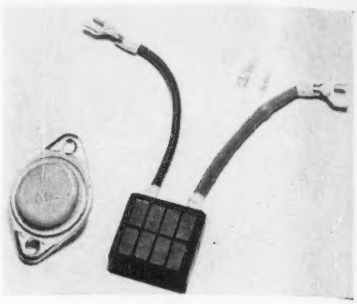
A Corrosion Control Short Course will be held October 3-5 in conjunction with the 1960 Western Region Conference in San Francisco.



THERMOELECTRIC MODULE known as a Frigistor with eight thermocouples is shown above with a typical germanium transistor for size comparison. Fabricated of Neelium, a new semiconductor material, the Frigistor produces thermal energy from electric power with no moving parts.

Kits Available for Studying Principles Of Thermoelectricity

Experimental kits designed for studying basic thermoelectric principles are available. Containing the necessary parts for thermoelectric cooling experiments, the kits can be used by schools and colleges.

Thermoelectricity, the science of producing thermal energy from electric power with no moving parts, is applicable to a variety of cooling and heating functions in electronics, biology, medicine, food and chemical processing and in the basic commercial fields of air conditioning and heating for homes, buildings and automobiles.

Basic unit in the kit is a thermoelectric module known as a Frigistor, consisting of eight thermocouples fabricated from Neelium, a new semiconductor material (see accompanying photograph). The kit also includes two fin assemblies (one for use at the hot junction for heat dissipation and one for mounting transistors which require cooling), a thermocouple, a special heat conductive adhesive, an insulating material, a suitable power supply and a booklet to be used as a guide in calculating hot and cold junction temperatures and heat pumping capacities.

The phenomenon of thermoelectricity occurs when an electrical current is passed through a suitable semiconductor material. Current moving in one direction produces cooling; reversing the current produces heat.

The kits are marketed by General Thermoelectric Corp., P. O. Box 253, Princeton, N. J.

Continuous Rail Welding

Continuous-welded rails may be an important part of the railroad's modernization program. A new welding plant to produce continuous-welded rail on a contract basis was opened this summer at Harrisburg, Pa., by the Linde Company, Division of Union Carbide Corporation.

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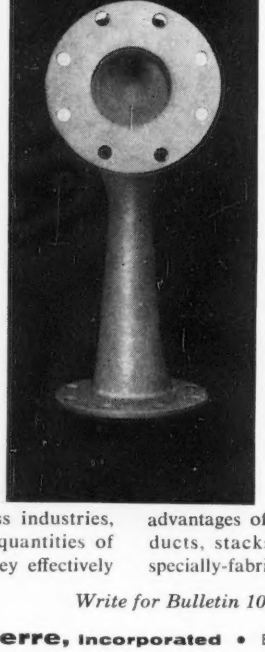
Western Region's 1960 Conference will be Oct. 6-7 at the Sheraton Palace Hotel in San Francisco, Cal.

Du Verre Completely Controls Corrosion in New S&K Gas Scrubbers



Now du Verre resin bonded fiberglass construction adds superior corrosion resistance to Schutte and Koerting's efficient Ejector-Venturi Scrubbers. Widely used throughout the process industries, SK 4010 units move large quantities of air and gas at low draft. They effectively remove dust and particulate matter, obnoxious vapors and corrosive gases.

Besides complete corrosion control, du Verre construction offers many other important advantages: Unlike lined equipment, venturi and jet can be accurately machined for more efficient operation. Erosive action of the high velocity venturi jet is minimized, even at temperatures approaching 300° F. High strength coupled with low weight eases handling and installation. The need for elaborate supporting steel is eliminated. Complete corrosion resistance on both exterior and interior surfaces eliminates need for painting and maintenance.

Investigate the many advantages of du Verre corrosion-resistant ducts, stacks, hoods, tanks, trays and specially-fabricated process equipment.

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New Finish Developed for High Carbon Steel Wire

A new surface finish designed to give twice the adhesion with as good corrosion resistance as present finishes has been developed for high carbon steel wire used in reinforcing rubber goods. The new coating provides better adhesion with wider variations in rubber compounding and longer storage life than other finishes, according to the manufacturer, National-Standard Co., Niles, Mich.

Applications have included reinforcing wire in bilge hose for nuclear submarines and bead wire for aircraft tires.

Research Group to Study Stainless Copper Problem

Development of a stainless copper by possible metallurgical surface treatment and development of organic and inorganic protective finishes for copper, brass and bronze are among proposed projects to be undertaken by the Copper and Brass Research Association.

Another proposed project is development of abrasion resistant plastic finishes for copper products and combinations of copper with newer plastics and glasses to give materials of superior properties and great esthetic appeal.

Forecasts Available On Pollution Outlook

Forecasts of prolonged periods of high air pollution potential for the eastern United States are being disseminated by the U. S. Weather Bureau Research Station at the Robert A. Taft Sanitary Engineering Center.

Persons in the study area interested in being alerted to occasions when large scale meteorological conditions are conducive to air pollution build up should contact their local weather bureau office.

New Plasma Spray Method

New spray and spray nozzle design techniques permit spraying of materials of lower melting temperatures than possible before with plasma spray devices.

The new technique permits spraying of epoxy powders. With melting points of only 300 F, epoxies were considered impossible for plasma treatment.

Such materials as zinc, lead or soft solder obtainable in powdered form also may be sprayed. High purity of the sprayed materials is maintained by operating the spray equipment with inert gases.

The new techniques were developed by Plasmadyne Corporation, 3839 S. Main St., Santa Ana, Cal.

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About 72 brands of cleaning products for use in the home were on sale at USA supermarkets in 1959.

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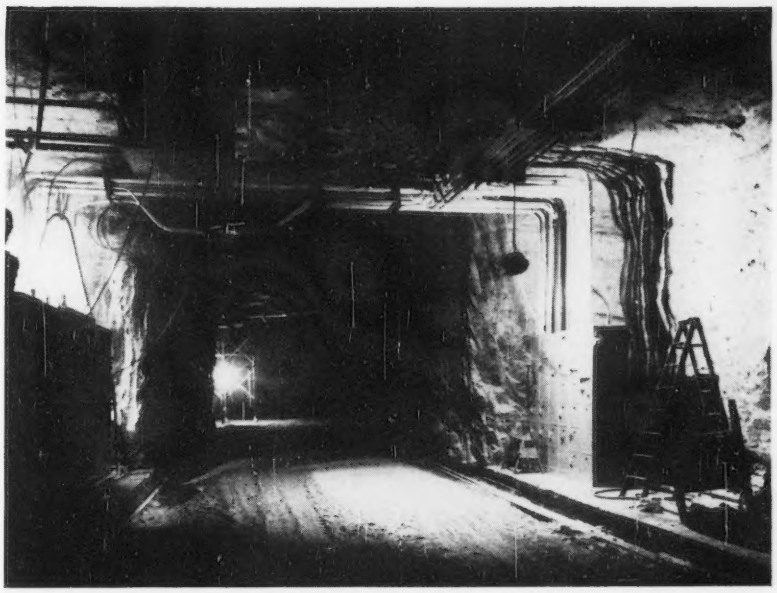
One American auto manufacturer offered 73 different models of its car for sale in the USA during 1959.



ALMOST 60,000 FEET of rigid aluminum electrical conduit has been installed in an Ohio salt mine for corrosion resistance. Although the temperature is a constant 74 F in the mine, the salt environment is a severely corrosive one for most uncoated metals. The aluminum conduit was installed without coating because of the metal's natural resistance to salt. The 2000-foot salt mine, considered to be the deepest in the United States and the first to be devloped in 25 years, is operated by Morton Salt Company. The conduit was supplied by Kaiser Aluminum & Chemicals Sales, Inc.

Computer Circuit Boards Coated With Epoxy Resin

New potting and protective coating techniques for complete computer subassemblies have been developed for protection against humidity, contamination, shock and vibration. The assemblies being given this coating are the printed circuit boards of electronic digital computers.

Because of its resistance to heat, cold and abrasion, epoxy resin is used as the protective material. One of its main advantages is that it can be applied at room temperature and set at temperatures low enough to prevent damage to the sensitive transistors, diodes, resistors and capacitors on the printed circuits.

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The 1960 North Central Region Conference will be held Oct. 19-20 at the Schroeder Hotel in Milwaukee, Wis.

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The 1960 South Central Region Conference will be held October 25-28 at the Mayo Hotel, Tulsa, Okla.

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Method Developed For Metal Plating Without Embrittlement

A new method of plating metal parts for corrosion protection has been developed which eliminates hydrogen embrittlement as a problem in plating high strength steel and which does not require baking of the parts to fuse the coating.

The coating operation is carried out in a standard, rubber lined tumbling barrel. After the parts are cleaned, the plating metal powders are added and covered with water. After the barrel is rotated for 45 minutes, the plated parts are separated from the impact media which can be washed and re-used. Water and spent chemicals are drained directly into the sewer without need of treatment, thus eliminating a disposal problem.

Other advantages of this method include plating thickness control, application of alloy coatings as simply as pure metals and mass plating of small metal parts and assemblies.

Thickness of plate is controlled by the quantity of metal powder added to the tumbling barrel. Coatings thicker than normal can be obtained with the same equipment and in approximately the same time by adding more plating metal powder.

Present commercial installations are applying zinc coatings, but the method is being tested for cadmium and other metals.

The method can be used also for mass plating small metal parts and assemblies, some of which could not be plated successfully by other methods because of design factors.

This new method was developed by Minnesota Mining and Manufacturing Co., St. Paul, Minn., and has been licensed to selected plants in the fastener, spring and powder metallurgy industries in the north central and eastern states.

ASM 42nd Metal Congress To Be Held October 17-21

Technical program for the 42nd National Metal Congress to be held October 17-21 in Philadelphia will be divided into two major classifications: scientific aspects of metals and practical engineering aspects of materials and processes.

Papers of probable interest to corrosion engineers will include the following: "Cause or Nature of Corrosion Failue," by B. H. Brown, U. S. Naval Research Laboratory, "Evaluation of Corrosion Performance," by R. J. Landrum, E. I. duPont de Nemours & Co., "Influence of Microstructural Features on Corrosion Resistance of Several Metals and Alloys" by A. M. Hall and W. K. Boyd, Battelle Memorial Institute, "Brazing of Stainless Steel Assemblies" by H. M. Webber, Harper Electric Furnace Corp., "Vacuum Furnaces for Processing Stainless Steels" by Gerbert Westeren, C. I. Hayes, Inc., "Preferential Corrosion of Stabilized Stainless Steel Welds" by C. L. Angerman and P. Kranzlein, E. I. duPont de Nemours & Co., and "Mechanism of Rapid Intergranular Oxidation of 18 Cr-8 Ni Stainless Steels by Oxygen and Dry Sodium Chloride in the Temperature Range 1100-1400 F" by M. G. Fontana, F. H. Beck and H. W. Pickering, Ohio State University.

Galvanizers' Meeting

The Galvanizers Committee of the steel industry, sponsored by the American Zinc Institute, will hold its 42nd meeting on October 27-28 at the Onesto Hotel, Canton, Ohio. The committee consists of technical and operating representatives of major steel producers in the United States and Canada who are engaged also in galvanizing sheet or pipe.

FOCUS ON PLASTICS IN PROCESS EQUIPMENT

Five articles on plastic applications for process equipment will be featured in the Technical Topics for November as part of that issue's special "Focus on Plastics in Process Equipment." Titles of these articles are given below.

Another feature of the "Focus on Plastics" in the November issue will be publication of a report of NACE Task Group T-4B-5 on Non-Metallic Sheaths and Coatings. The report is entitled "Practices and Experience With Protective Jackets for Outside Plant Lead and Aluminum Sheathed Cable."

Articles to be published in the November issue's Record and Report Section also will include information on plastics used for corrosion control. These articles will deal with vinyl coated exhaust stacks, reinforced plastic pipe for handling corrosive wastes, a new polyvinyl dichloride that can be used in industrial hot-acid piping and reinforced polyester panels used to prevent corrosion of industrial building sidings.

Technical Topics for November are as follows:

Some Results from Elevated Temperature Testing of Polyester Castings and Laminates, by S. S. Feuer and A. F. Torres.

Laboratory Testing of Spay Applied Lining Materials, by R. S. Foster.

Design Considerations for Applying Reinforced Plastics in Corrosive Environments of the Process Industry, by Fred W. Arndt.

Case Histories Indicate Tetrafluoroethylene Lined Pipe Has Lower Installation Cost Than Other High Temperature Piping, by T. R. Thierry.

Characteristics, Testing and Some Design Considerations Applicable to Glass-Reinforced Plastic Pipe, by R. M. Levy.

Sources Given for Russian Literature On Corrosion Topics

Several sources of Russian corrosion literature are listed below, and references are made to past issue of CORROSION Magazine giving information on the availability of Russian and other foreign literature dealing with corrosion topics.

Most Russian technical articles on corrosion appear in the following three publications: (1) *Journal of Applied Chemistry* (Zhurnal Prikladnoi Khimii), which is translated completely in English beginning with the 1958 issue and is available from Consultants Bureau, 227 W. 17th St., New York 11, N. Y., (2) *Journal of Physical Chemistry* (Zhurnal Fizicheskoi Khimii) and (3) *Science of Metals and Working of Metals* (Metallovedenie i Obratotka Metalloy).

Many articles on corrosion are published in various publications of the Russian Academy of Sciences (Akademiia Nauk), particularly the *Transactions of the Committee for Combatting Corrosion of Metals* (Trudy Komissii po Bor'be s Korroziei Metalloy), which deals exclusively with corrosion material.

Other publications of the Academy are the *Electric Power Stations* (Elektricheskie Stantsii), *Bulletin of Machine Construction* (Vestnik Mashinostroeniya), *Gas Industry* (Gazovaya Promyshloennost) and *Industrial Laboratory* (Zavodskoya Laboratoria) which is available in complete English translations beginning with the 1958 issue from the Instrument Society of America, 313 Sixth Ave., Pittsburgh 22, Pa.

A monographic series begun in 1954 which deals exclusively with corrosion is *Corrosion in Chemical Industry and Protection Against It* (Korroziia v Khimichestikh proizvodstvakh i sposoby Zashchety ot nee).

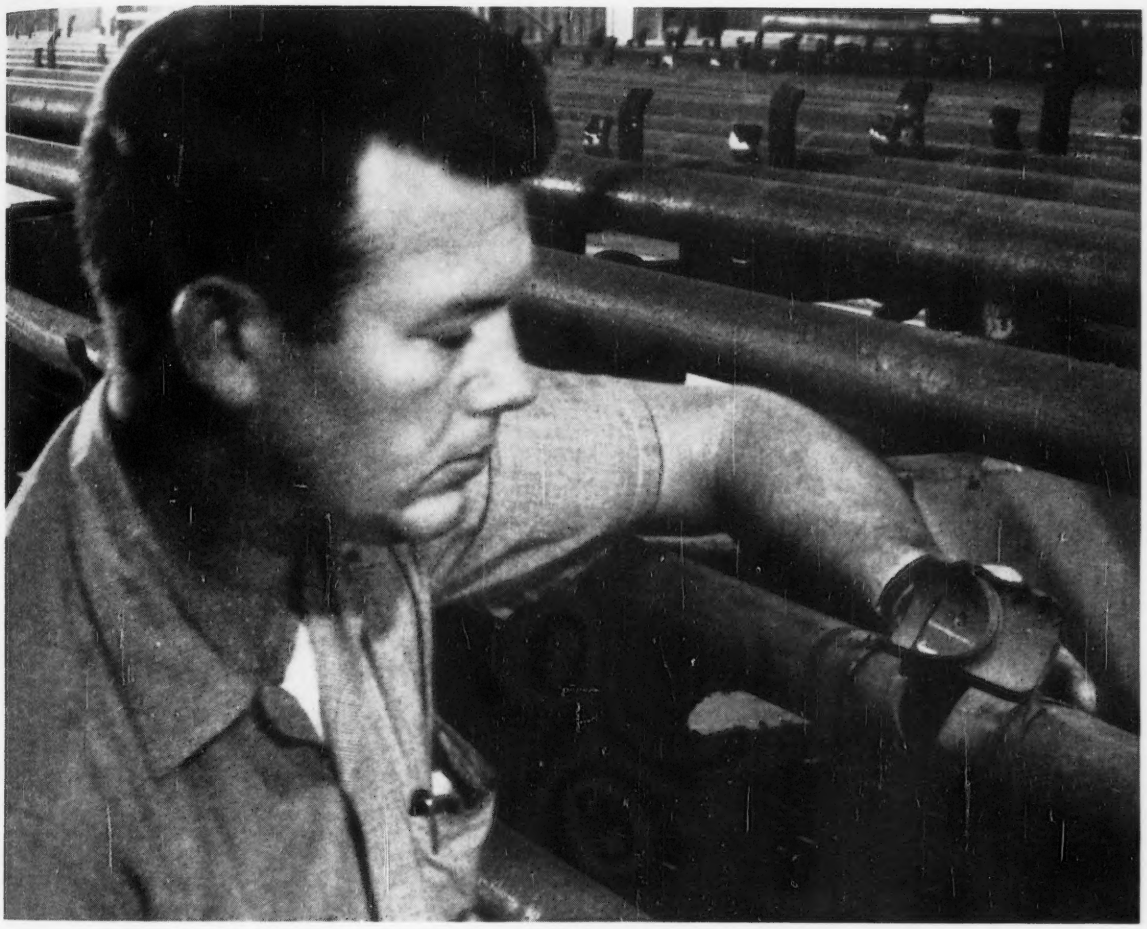
Other Russian technical journals that are available in the United States in full English translations are the following: *Journal of General Chemistry of the USSR, Bulletin of the Academy of Sciences of the USSR—Division of Chemical Sciences, Proceedings of the Academy of Sciences of the USSR* and the *Metallurgist*.

Additional information concerning foreign technical publications and translations services can be found in two prior issues of CORROSION. On Page 46 of the February, 1960, issue are listed Russian titles of publications with names and addresses of U.S. institutions and persons providing translations and abstracts.

On Page 77 of the October, 1959, issue of CORROSION, references are given to information published in previous issue on foreign technical articles, many of them Russian. These issues in 1958 were March, May, June, August, October and November. In 1959, information is given in the February and April issue.

Alloy Data Sheets Available

Detailed information on alloys for abrasion, impact, corrosion and heat resisting services is given in a series of data sheets issued by Coast Metals, Inc., Redneck Ave., Little Perry, N. J. Each sheet provides engineering data on a single alloy including available forms, physical properties, nominal chemical composition, typical applications and recommended finishing procedures.



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Eleven Papers to Be Given at October 5 Plastics Meeting

Eleven technical papers on the theme "Plastics Versus Corrosion" are scheduled for presentation at the October 5 regional conference of the Society of Plastics Engineers to be held at the Mark Hopkins Hotel, San Francisco, Cal. Titles of papers are given below.

Additional information can be obtained by writing Conference Chairman J. W. Richardson, Rohm & Haas Co., 600 California St., San Francisco, Cal.

Trends in Plastics as Materials of Construction for Corrosion Resistant Applications, by Raymond B. Seymour, Sul Ross State College, Alpine, Texas.

Combatting Corrosion With Butyrate Pipe, by W. P. Gideon and Roy O. Hill, Jr., Eastman Chemical Products, Inc.

Polyesters as Corrosion Resistant Coatings, by Lawrence Graubart, Reichhold Chemicals, Inc.

Uses of Penton Chlorinated Polyester as a Chemical Resistant Plastic, by John Lomax, Hercules Powder Co.

Real Facts About Vinyl Maintenance Coatings, by David A. Bisson and William H. McKnight, Union Carbide Plastics Co.

A New System of Large Structures of Glass Fibers and Polyester, by John Heidacher, Studebaker-Packard Corp.

Use of Thermoplastic Piping Systems for Corrosion Service, by Jack G. Fuller, Jr., Chemtrol.

High Density Polyolefins—Their Application in Corrosion Engineering, by O. E. Larsen, Phillips Chemical Co.

Vinyls in Corrosive Applications, by E. B. Osborne, B. F. Goodrich Chemical Co.

New Pumps from Old, Via Plastics, by Isadore Nusbaum and S. E. Susman, Narmco Industries, Inc.

Corrosion (a film on corrosion protection of steel pipe with plastic materials) presented by S. M. Robertson, Koppers Co., Inc.

Wisconsin University Sets Five Engineering Meetings

Schedule of several engineering meetings for this fall have been set by the Engineering Institute of the University of Wisconsin. Specialists from research laboratories, consulting firms and the university faculty will present informal talks, panel discussions, films, slides and demonstrations to help keep engineers abreast of the rapidly changing technology.

The schedule includes the following meetings:

Plastics: Basic Chemistry and Technology, Oct. 19-21; Plant Engineering, December 8-9; Sanitary Engineering, Jan. 10-11; Technical Report Writing, Jan. 25-27 and Non-Destructive Testing, Jan. 26-27.

Detailed program announcements and registration information can be obtained from the Engineering Institute, 4020 Stadium, Madison, Wis.

Indian Institute of Metals

The 14th Annual Technical Meeting of the Indian Institute of Metals will be held December 1-4 at Bhilai. The 7th Metallographic Contest and Exhibition also will be held during the meeting. Plant visits will be included as part of the program.

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Would you like a binder that will permit you to keep issues in sequence?

Provided there is sufficient interest by CORROSION readers, binders that will hold 12 issues will be available at nominal cost. Issues are held securely by a steel wire that fastens into the binder. This permits you to keep the binder upright on your desk, or in a book case. Copies are not damaged by the attachment and may be removed for permanent sewed binding if desired. This offer is contingent on a sufficient number of orders being received by CORROSION before October 1.

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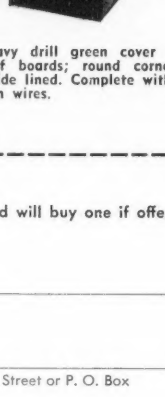

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New Gun Designed to Spray Asphalt and Fiber Films

A spray gun that can be used for applying asphalt or other materials and chopped glass fibers simultaneously to produce a single monolithic film. Called the Monoform System by Flintkote Company, 30 Rockefeller Plaza, New York 20, N. Y., it can be used for applying roofing, sidewalls or insulation, pipe coatings and coatings for protection of water tanks.

A pump and compressor force the coating material through hoses. A special gun with three nozzles is used: one for glass fibers and two others for coatings. The gun applies the formulated emulsions with a continuous flow of chopped fibers. These may be combined with other aggregates including crushed rock, vermiculite, sand, roofing granules, metallic powders and decorative flakes.

Conference on Lighthouses To Be Held in Washington

The Sixth International Technical Conference on Lighthouses and Other Aids to Navigation will be held in Washington, D. C., during the week of September 26. Corrosion is not a featured subject but will be discussed in some of the 150 presentations such as "Modern Methods of Buoy Preservation" and "Various Uses of Plastics Construction."

A booklet containing abstracts of papers to be presented can be obtained by writing Captain J. A. Ciccolella, U. S. Coast Guard, Washington 25, D. C. Application for registration at the conference also can be made through Captain Ciccolella.

German Standards Printed In English Translations

German standards translated into English have been published by Deutscher Normenausschuss, Uhlandstrasse 175, Berlin W 15, Germany. Those standards of probable interest to corrosion engineers are listed below:

Non-Ferrous Metals: 1701 Refined nickel, 1702 Nickel anodes and 1706 Zinc.

Plastics: 7743 Plastics; types of moulding materials, cellulose acetate butyrate (CAB) injection moulding materials.

Testing of Plastics: 53388 Testing of Plastics; determining resistance to light; 53445 Sheet 1—torsion pendulum test (preliminary standard).

Insulating Materials: 49020 Conduit for electrical wiring; screwed steel conduit, plain conduit, couplers.

New Study Technique Found For Superconductivity

A new technique for study of superconductivity has been developed at the General Electric Research Laboratory, Schenectady, N. Y. Superconductivity is a property of certain materials in which all resistance to passage of an electrical current disappears at temperatures near absolute zero (459 degrees below zero, Fahrenheit).

The new method permits direct visual observation of transformations between the normal and superconductive states. Superconductive devises are expected to find important applications in electronic computers, missile and aircraft guidance and control systems and other electronic units.

German Digest Published on U. S. Water Conservation

"Wasserversorgung In USA," a 100-page book in German, digests the findings of a group of German workers in the water conservation field in a 1958 survey of water conservation practices in the United States. Included among the places and organizations on itinerary of the scientists were Philadelphia, Dallas, Lansing, Mich.; U. S. Public Health Service, Bethlehem Steel Foundry, Burlington, N. J., and several technical organizations, including NACE.

The book was published by Landeshauptstadt Munchen, Mullerstrasse 18, Munchen, Germany.

Technical Papers to Be Published in December

Effect of Various Curing Agents on Chemical Resistance of Epoxy Resins, by Ronald L. DeHoff

Internal Carburization and Oxidation of Nickel-Chromium Alloys in Carbon Monoxide, by B. E. Hopkinson and H. R. Copson

Ship Coating of Structural Steel, by John D. Keane and Joseph Bigos

Impressed Current Anodes for Cathodic Protection, by Walter P. Noser

High Temperature Corrosion in Refinery and Petrochemical Service, by E. N. Skinner, J. F. Mason and J. J. Moran

Inhibition of Corrosion of Commercial Aluminum Alkaline Solutions, by J. Sundarajan and T. L. Rama Char

X-Ray Techniques Used to Check Porcelain Valves

X-ray techniques similar to those used by doctors to check the human body are now applied by ceramic engineers to check porcelain valve bodies. Potential faults in the valves can be caught that might lead to failure in field service.

Greater reliability in locating deep seated flaws has been experienced with the use of X-ray test than with the older method of testing by high voltage flash-over.

The X-ray test method is being used by Lapp Insulator Co., 119 Hall St., LeRoy, N. Y.

New Orleans Engineering Meeting Set Sept. 18-21

Five papers of probable interest to corrosion engineers will be presented during the 15th Annual Petroleum Mechanical Engineering National Conference to be held September 18-21 at the Jung Hotel, New Orleans, La. The conference is sponsored by ASME.

The papers include the following: Evaluation of Glass Reinforced Plastic Pipe, Aluminum in the Petroleum Industry, Bi-Metallic Pipe, Use of Copper Alloy Tubes in the Petroleum Industry and Ultrasonic Testing.

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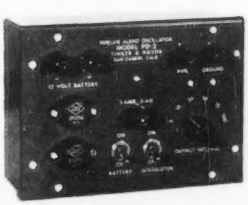

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The Surface Chemistry of Metals and Semiconductors

Edited by HARRY C. GATOS, *Associate Head, Solid State Division, Lincoln Laboratory, M.I.T.; with the assistance of* J. W. FAUST, JR., AND W. J. LA FLEUR.

This unique volume contains the carefully edited papers presented at the Joint Symposium of the Corrosion and Electronics Divisions of The Electrochemical Society on the Surface Chemistry of Metals and Semiconductors, sponsored by the Office of Naval Research and The Electrochemical Society, Inc. It meets the compelling need for integration of the present knowledge of metal and semiconductor surfaces.

Metal and semiconductor surfaces have many common characteristics, yet the study of these two fields has been along widely different lines. Because there is now a definite need to expand both fields of study, this book correlates the striking progress in semiconductor theory with the advanced technology of metal surface research. The result is an effective interchange of theory and technology that broadens understanding of surface behavior.

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III. Electrode Behavior of Metals and Semiconductors
IV. Surface Reactions in Liquid Media
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BOOK NEWS

Cleaner Air for North Carolina. By Billy C. Blakeney and Marvin D. High. 62 pages, 8½ x 11 inches. 21 July, 1960. Dept. of Health, Education and Welfare, Public Health Service, Robert A. Taft Sanitary Engineering Laboratory, 4676 Columbia Parkway, Cincinnati 26, Ohio. Free.

A comprehensive survey of the air pollution and control problem of North Carolina. Contents include meteorology, sources of pollution, effects, results of air sampling program, summary of air pollution activities, air pollution legislation and control program. Appendices include: Air Pollution legislation by other states, guiding principles, air pollution legislation and survey forms. There are 49 references.

Materials Selection for Process Plants. By R. E. Gackenbach. 318 pages, 6 x 9, cloth. July, 1960. Reinhold Publishing Corp., 430 Park Ave., New York 22, N. Y. Per copy, $8.50.

A readable discussion of the principal programs facing the engineer concerned with materials selection. Contents include:

Corrosion and Corrosion Phenomena: Covers the various kinds of corrosion, their causes and some remedies.

Cathodic Protection: A brief summary of the theory and application.

Inhibitors: Enumeration of the principal kinds and their mechanism.

Design: Factors which can prevent or reduce corrosion are explained.

Materials: Iron and steel, cast irons, wrought irons, alloy castings, stainless steels, medium alloys, high alloys, aluminum and aluminum alloys, copper and copper alloys, nickel and nickel alloys, lead and alloys, exotic metals and alloys, brick construction, plastics, rubber and elastomers, paints and coatings.

There is a glossary of corrosion terms (compiled by Inter Society Corrosion Committee of NACE); glossary of mettalurgical terms, and an alphabetical subject index.

3rd Metallurgy Symposium on Corrosion, Aqueous and Gaseous. (In French) 239 pages, 8¼ x 10¾ inches, cloth. North-Holland Publishing Co., P. O. Box 103, Amsterdam, Holland. Per copy, $10.

A collection of the papers presented at the symposium 29-30 June-1 July, 1959. All titles are translated into English and each article is preceded by an abstract in English and French.

Titles include: Recent development of ideas of the oxidation of metals, attack on graphite by gaseous impurities in a high temperature, helium-cooled graphite moderated reactor; diffusion mechanisms and gaseous corrosion.

Corrosion inhibition of magnesium in wet air by surface fluoration, selection of alloys to resist high temperature corrosion, magnesium and uranium ignition in gaseous atmospheres, oxidation film morphology, corrosion of stainless steels in aqueous solutions, influence of hydrogen on the corrosion of zirconium and its alloys in high temperature water, precipitation of chromium carbide responsible for intercrystalline corrosion in austenitic stainless steels, corrosion of stainless steels by high temperature pure water, stress corrosion cracking of Inconel in high purity water, stress corrosion cracking of Inconel in high purity water, "knife-edge" corrosion of stainless steel welds, use of potentiostat in studying the behavior of metals in liquids, intergranular corrosion of 18-8 stainless steel, results obtained at Biarritz seawater testing station, fixation of radioactive sulfur on the surface of iron—influence in electrochemical corrosion; present state of knowledge on corrosion of steels by hydrogen sulfide.

The book is liberally illustrated, contains numerous tables of data and references.

Korrosion 12. 264 pages, 8¼ x 11⅝ inches, paper. In German. 1960. Proceedings of the 2nd Congress, European Corrosion Federation, Frankfurt am Main, 31 May-8 June, 1958. Verlag Chemie, GMBG, Weinheim/Bergstr. Germany. Per copy, DM 36.

A wide variety of information on corrosion processes and corrosion prevention presented at the 1958 meeting of the European Corrosion Federation at Frankfurt. Included among the section headings, water and atmosphere, chemical technique, electrochemical reactions, testing, indexing. The papers cover corrosion and passivity, soil, tinplate, stress corrosion, galvanic corrosion, pitting, lead piping, titanium, cast iron, plastics, inhibition, paint films, sprayed zinc and aluminum, ceramic coatings, corrosion products, electrochemical measurements, documentation and others.

The book is liberally illustrated with line and halftone figures and has numerous tables of data.

PERIODICALS

Chemical Titles. Bi-monthly. First issue scheduled, January 1961. The American Chemical Society, 1155 Sixteenth St., N. W., Washington 6, D. C. Non-member rates (24 issues, one volume) 1-10 subscriptions, each $65; school and ACS members, $50. Reduced rates for additional subscriptions.

An ingenious use of the capabilities of a computer for handling rationalizing and indexing information is exemplified in this periodical to be issued first in January, 1961. Using a punch card input, the machine prepares titles and authors of significant articles from over 500 journals concerned with chemical matters in the following form:

1. A keyboard index. This index consists of permutations of the keywords in the titles, with remainder of the titles arranged before and after the keyword to afford examination of context. This index is divided into two parts: General chemistry and biochemistry.

Coded in the same line with the title is the first four letters of the first author's name, year of publication plus initial letters of first three keywords that are to be permuted.

2. A first author index. This index includes names of all authors and complete title and reference.

3. An alphabetical author index.

4. List of general periodicals and list of biochemical periodicals.

Three periodicals dealing with corrosion are included, one each from the United States, France and England.

Over 250,000 fibers of glasslike iron silicate guard each cross-sectional square inch of wrought iron pipe against corrosion

Now—4-D Wrought Iron Pipe assures even longer service life

There's a practical, fool-proof way to evaluate a piping material's potential in corrosive service: check its performance under actual field conditions.

The photo above shows how standard wrought iron pipe measures up when this service-life yardstick is applied. Here you see actual samples taken from wrought iron pipe installations in a variety of corrosive services. Some of these sections came from buildings that were being torn down. Some were cut from in-use installations by our laboratory staff. They tell a convincing story of piping longevity.

Now, new 4-D Wrought Iron is available to further augment the qualities of *standard* wrought iron, known for decades as the optimum in corrosion resistance. And increased corrosion resistance, improved mechanical and physical properties and greater uniformity widen the gap between 4-D Wrought Iron and ferrous substitutes. In-service and comparative laboratory tests support this conclusively.

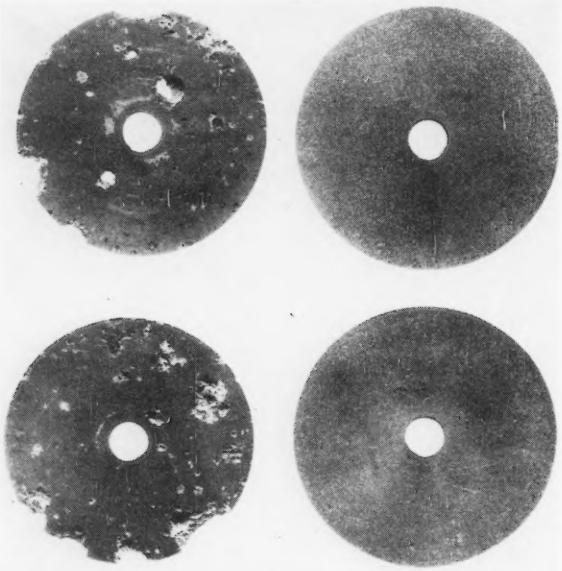
Ask the Byers representative to relate the advantages of new 4-D Wrought Iron to your corrosive applications. And write us for new 4-D Wrought Iron literature and test data. A. M. Byers Company, Clark Building, Pittsburgh 22, Pennsylvania.

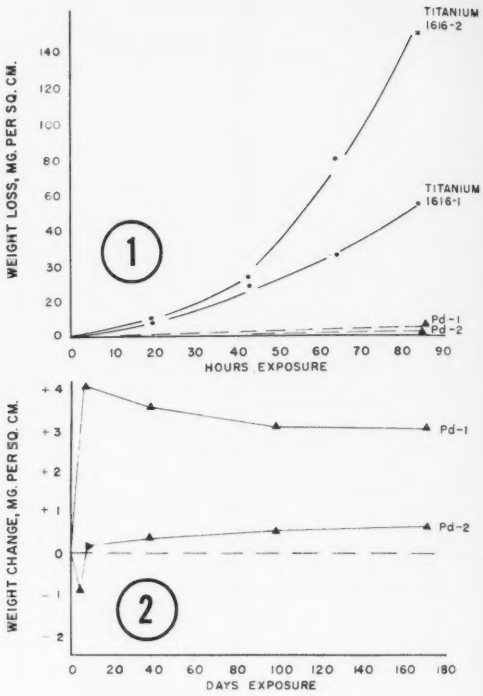
BYERS 4-D WROUGHT IRON

TUBULAR AND FLAT ROLLED PRODUCTS

ALSO AMBALLOY ELECTRIC FURNACE STEELS AND PVC PIPE AND SHEET

Corrosion costs you more than Wrought Iron





TITANIUM-PALLADIUM ALLOY specimens on the right showed no corrosion after exposure to 73 percent boiling calcium chloride. Unalloyed titanium specimens on the left were pitted and perforated. Graph 1 shows the resistance of the titanium and titanium-palladium specimens to boiling 5 percent sulfuric acid. Graph 2 gives the resistance of the titanium-palladium alloy to 5 percent boiling sulfuric acid for a longer exposure.

Titanium-Palladium Tests Show Alloy's Corrosion Resistance

Corrosion resistance of titanium-0.2% palladium alloy has been confirmed by recent tests in reducing type environments at a nuclear research laboratory and in a chlorine chemical plant.

Samples of commercial titanium and titanium-0.2% palladium alloy were suspended in 5 percent boiling sulfuric acid. The commercial titanium was removed after 85 hours because of excessive corrosion, but tests on titanium-palladium alloy were continued for 170 days and showed a low corrosion rate (see Graph 1 above). As shown in Graph 2, the corrosion rate did not increase with time. The alloy was virtually free from corrosion throughout the test.

In the chlorine chemical plant tests, specimens of both metals were placed in a stream of boiling, non-aerated 73 percent calcium chloride for 84 days. The titanium-palladium alloy samples were unaffected; the unalloyed titanium was badly pitted and perforated as shown in the photograph above.

Tests were conducted at Argonne National Laboratory, operated by the University of Chicago for the Atomic Energy Commission, and at Columbia-Southern Chemical Corp., Barberton, Ohio.

1960 Corrosion Show Color Slide-Talk

A show consisting of 108 color slides has been prepared showing some of the exhibits at the March 15-17 Dallas exhibition. This 1960 Corrosion Show color slide presentation will be accompanied by a commentary describing the exhibits and many of the items displayed.

NACE Section program chairmen who are interested in using this in one of their programs may make bookings by writing to G. A. Rolak, 1061 M & M Bldg., Houston 2 Texas.

The show gives members who were unable to attend the conference an opportunity to see some of the exhibits at what many have said was the best Corrosion Show held so far.

NBS Installs New Electron Accelerator for Research

A particle accelerator producing one of the world's most intense high-energy electron beams will be installed at the National Bureau of Standards new laboratory facility at Gaithersburg, Md. The accelerator will be used for basic data, standards and measurement techniques needed in the new branch of radiation physics.

Pure Beryllium Tubing Now Available in United States

Pure beryllium tubing, a material with promising applications in nuclear reactors, aircraft and missiles, will be available in the United States under terms of a technical exchange agreement with Chesterfield Tube Company, Chesterfield, England.

In nuclear applications, pure beryllium tubing has the advantages of low density, high rigidity, compatibility with hot carbon dioxide and good oxidation resistance at temperatures to 1500 F.

The agreement was made with Superior Tube Company, Norristown, Pa.

Jet Aircraft Do Not Add To Air Pollution Problem

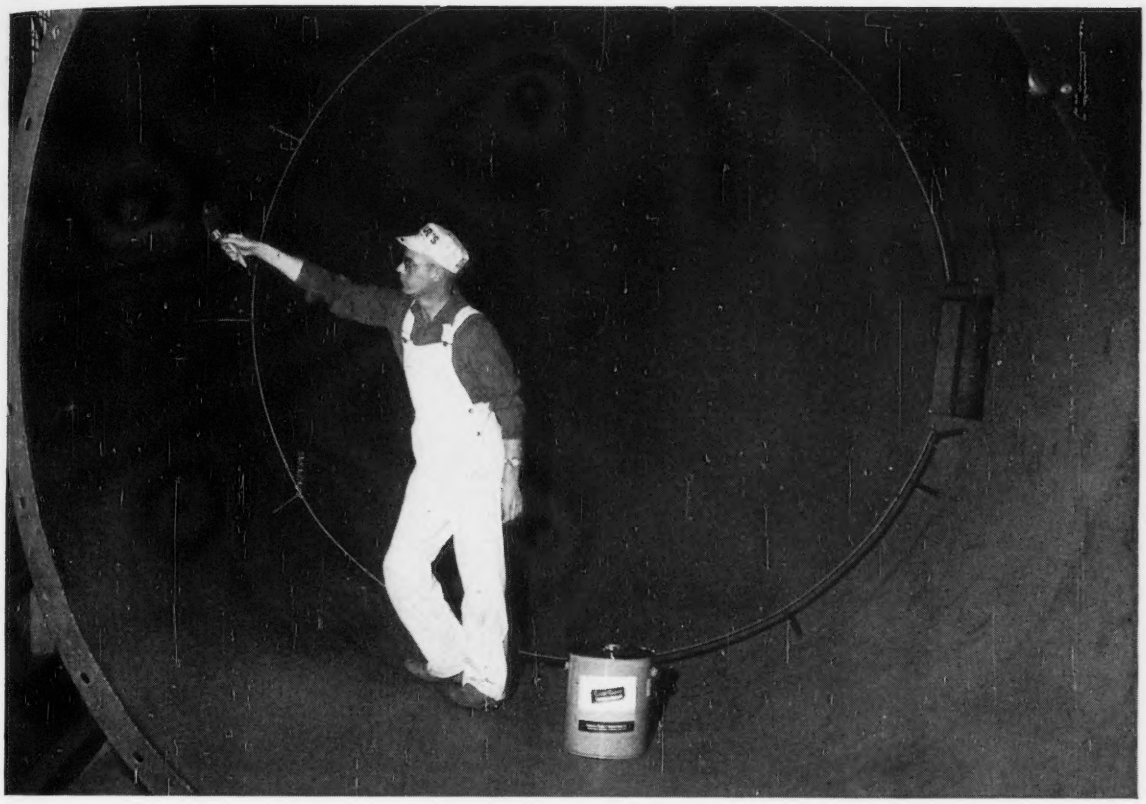
Jet aircraft are not contributing to the smog problem in the Los Angeles area, according to the Air Pollution Control District. Total daily pollution from all commercial jets operating at less than 3500 feet over Los Angeles County, including ground operations, was determined to be insufficient to cause eye irritation, plant damage or visibility reduction.

Although jet traffic by 1965 is expected to increase 475 percent, the additional pollution will not be of significance in the smog problem.

Wrought Iron Pipe Gives 30-Year Corrosive Service

Standard weight, 2-inch wrought iron pipe removed from a private school in Cincinnati showed no corrosive attack after 30 years' service. Two wrought iron lines were removed from the school: one a steam line, the other a condensate return line. Both were in use 30 years and were pulled for relocation of new lines during rennovation of the building.

Wrought iron has been specified for new steam and condensate return lines. The old wrought iron piping was in such good condition that it is to be re-used for sleeves and miscellaneous piping.



Tank of exhaust gas washer, made by Iowa Manufacturing Co., for use in air pollution control. Neoprene-based coating, used to protect tank from abrasion and corrosive acids, is applied to all interior metal surfaces.

In high-velocity exhaust gas washer...

NEOPRENE COATING GIVES LASTING PROTECTION AGAINST ABRASION AND HOT SULFURIC ACID

Officials of the Iowa Manufacturing Company estimate that this exhaust gas washer tank will serve indefinitely, given proper maintenance. Previously, life span for their unprotected tanks was less than a year. What has made the difference? A protective coating of abrasion and acid-resistant Du Pont neoprene.

The company experienced severe corrosion problems on units installed in asphaltic concrete plants before finding this solution. Their washers, used for the control of air pollution, employ high-pressure water sprays to remove dust and sulfur dioxide before the exhaust gases are discharged. Inside the tank, water sprays cool the hot (300°F.) sulfur dioxide and trioxide gases and form sulfuric acid. A 5 mil neoprene coating protects the steel tank from this corrosive acid and high-velocity dust-bearing gas.

Neoprene's unique combination of properties includes proven, dependable resistance to abrasion and acids as well as to flame, oil, grease, weather, sunlight, heat, chemicals and ozone.

For information to help solve your corrosion problems, write for a copy of PROTECTIVE COATINGS AND LININGS. E. I. du Pont de Nemours & Co. (Inc.), Elastomer Chemicals Department C-9, Wilmington 98, Delaware.

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REG. U. S. PAT. OFF.

NEOPRENE
SYNTHETIC RUBBER

Better Things for Better Living... *through Chemistry*

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IN CORROSION PREVENTION
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FOrest 1-1861
6001

NEW PRODUCTS

Aluminum

A 5/8-inch lock on four sides is one feature of a 9 by 18-inch aluminum shingle being manufactured by Shingles, Inc., and distributed nationally by Aluminum Lifetime Shingle Co., both firms of Dallas, Texas. Stamped from cold roll, the shingles contain interlocking flashings such as starter strip, gable, end wall, valley, counter flashing, hips and vents of the same aluminum alloy.

•

Corrosion resistance, strength and light weight characteristics of aluminum alloy met the primary specifications and complicated problems of building an all-welded, aluminum hulled sailing yacht which recently captured first place in her class in the Newport to Bermuda race. This 58-foot yawl was built of Alcoa aluminum by the Burger Boat Co., Manitowoc, Wis.

Cleaners

Dissolution and removal of rust particles from most metals without changing the metal's dimensions is claimed for a new rust remover called Cor-o-dex, available from Allied Products Company 1133 W. Newport Ave., Chicago 13, Ill. The cleaner can be applied to metal surfaces by brush, spray gun, cloth or by immersion. Said to be effective on iron, steel, stainless steel, brass, bronze, copper, nickel and aluminum, the cleaner penetrates small cracks and unusual shapes, according to the manufacturer.

•

Removal of scale deposits from ice making machines is one of the recommended uses of non-staining liquid acid called Calgon liquid ice machine cleaner. It is made from a food grade phosphoric acid and can also be used to clean coffee urns and steam irons, according to the manufacturer, Calgon Company, Hagan Center, Pittsburgh 30, Pa.

Coatings, Inorganic

A single coat, inorganic zinc system designed to give galvanic protection and prevent rusting of fire water tanks has been developed by the Carboline Company, 32 Hanley Industrial Court, St. Louis 17, Mo. Called Carbo Zinc 11, the system is applied as a one-coat protection over commercial sandblasted steel. It is claimed to have a curing time of only three hours, becomes water insoluble in 20 minutes after application and can be applied in adverse weather conditions at temperatures as low as zero degrees F and in humidities as high as 100 percent without affecting its physical properties.

•

For protection of metal at constant heat at temperatures to 1400 F and in service requiring resistance to severe corrosive environments, the Dampney Company, Hyde Park, Boston 36, Mass., has developed a line of silicone and silicone-ceramic coatings. Bulletin 1570 describing the coatings and suggesting proper uses is available from the company.

Coatings, Organic

Combining the fast drying advantages of lacquer and the superior hiding power and durability of enamel, a new lead-free alkyd enamel is available in self-spraying aerosol containers. It is a vinyl-modified alkyd enamel developed by chemist Rudy Albrecht of the firm Seymour of Sycamore, Box 610, Sycamore, Ill. The enamel dries in 10 minutes and a second coat can be applied in 10 minutes without lascquer's tendency to lift sub-coatings, according to the firm.

•

Two coatings have been added to the line of protective coatings applied by the Nowery J. Smith Co., 8000 Hempstead Highway, Houston, Texas. One of them is known as Columbia 7, designed especially for use as a tank lining. The other is a PVC plastisol which is designed for corrosion and abrasion resistance under severe conditions such as exposure to acids, bases, slats, fumes and salt spray.

•

Increased vapor resistance of water soluble resin paints by addition of wet ground mica is explained in Technical Bulletin No. 42, available from the Wet Ground Mica Association, Inc., 420 Lexington Ave., New York 17, N. Y. Tests have shown also that there is increased resistance to permeation by solvents such as xyol when the mica is added to paint.

Inhibitors

A maintenance service program to give users periodic checks on the condition of their industrial engine radiators will be part of the service offered by Dow Chemical Co., Abbot Roads Bldg., Midland, Mich., in marketing its inhibitors for industrial engine cooling systems. After the inhibitor system has been in operation 12 to 14 hours, a sample is sent to Dow which will be analyzed and filed for reference. Periodic samplings sent in by the user will give Dow an opportunity to make recommendations after sample analysis for servicing the coolant to maintain maximum effectiveness for rust and corrosion control.

•

Prevention of tarnish and oxidation on copper and cadmium for several years, despite high humidity or intensive corrosive atmospheres, is claimed for new volatile corrosion inhibitor papers produced by Daubert Chemical Co., 4700 South Central Ave., Chicago, Ill. Known as Daubrite, the packaging papers need not contact the wrapped surfaces and do not have to be tightly sealed to give protection, according to Daubert Chemical. Subsequent operations on the packaged item such as soldering, brazing or plating will not be affected by the papers.

•

Five bulletins and brochures on corrosion inhibitors are available from Nalco

(Continued on Page 52)

how to keep metal away from petroleum . . .

UNICOR®

. . and why it pays, in terms of both product and equipment!

Petroleum products and metals are apt to wage war. Life-robbing corrosion attacks the metal, while profit-stealing contamination downgrades the product. But there's an easy way to forestall such trouble. Use UNICOR.

This potent, film-forming, oil-soluble corrosion inhibitor plates out on metal, stands off corrosion by crude or refined petroleum. Only 10 to 20 parts of UNICOR per million of product assures lasting protection against corrosion in pipelines, refinery vessels and tanks.

Purer product, longer equipment life, reduced downtime for maintenance and cleaning, lower power costs . . . all result from using UNICOR. For detailed information and samples write our Products Department.

See our PSE*

Correct selection and most effective use of petroleum inhibitor and additives involves expert analysis and consideration of many factors. As specialists for over a quarter-century, UOP is able to provide unparalleled field service, brought to you by a member of our staff of *Product Sales Engineers. For detailed information on the UOP family of superior inhibitors and additives call or write our Products Department.

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UNIVERSAL OIL PRODUCTS COMPANY

30 Algonquin Road, Des Plaines, Illinois, U.S.A.

WHERE RESEARCH TODAY MEANS PROGRESS TOMORROW

See why ALCOA ALUMINUM makes a good design habit

Requirement: Simple, low-cost heated lines to pipe high viscosity fluids
Key to Good Design: Specify UNITRACE and DUOTRACE, Alcoa's extruded aluminum pipes with integral steam chambers

With the development of UNITRACE® Piping, ALCOA created an entirely new technique for piping viscous fluids. Trace and product chamber are extruded in a single unit of light, strong, corrosion-resistant ALCOA® Aluminum. This integral steam-traced pipe eliminates the need for cumbersome, costly, inefficient pairing of separate pipes for steam and product. The resultant savings in initial cost are coupled with a major increase in the efficiency of heat application to the product piped.

Subsequent development of special flanges, elbows, adapter flanges and UNITRACE Trace Caps has made it possible to design and install completely integrated UNITRACE piping systems . . . compatible with standard piping components.

Now ALCOA has developed a new product, DUOTRACE,* to expand the design range of integrally traced piping systems. DUOTRACE contains not one but *two* trace chambers plus a product chamber in a single extruded aluminum pipe. This makes DUOTRACE the perfect solution to the need for recirculating tracing systems.

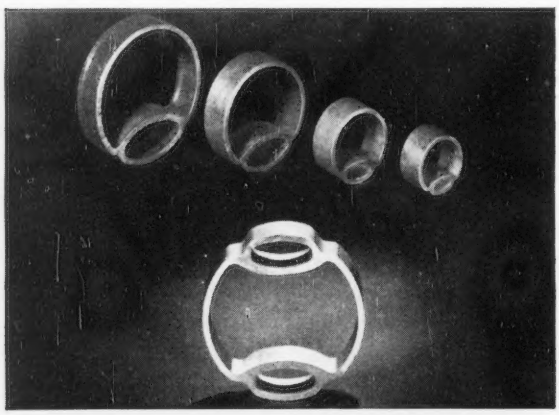
*Trademark of Aluminum Company of America

Today, the ingenuity of process industries designers has indicated intriguing new areas of potential use for both UNITRACE and DUOTRACE. Consider, for instance, the process economies which can result from the substitution of either UNITRACE or DUOTRACE for unit heat exchangers and preheaters.

Here you see an outstanding example of the way in which ALCOA is putting over 40 years of process industries experience to work to make aluminum your good design habit. You are invited to share that experience—through a series of engineering conferences which ALCOA is holding this year in a number of major cities. Your local ALCOA sales office will be happy to furnish details.

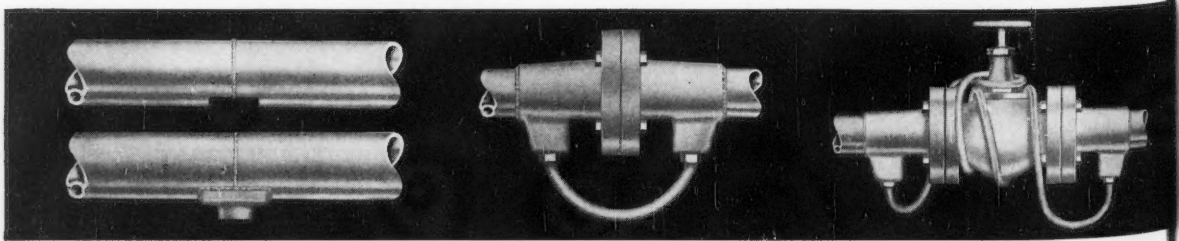
Take advantage, too, of the body of ALCOA literature which describes in technical detail the known performance characteristics of aluminum in a variety of process industries applications. Simply fill in and mail the coupon opposite. ALUMINUM COMPANY OF AMERICA, Alcoa Building, Pittsburgh 19, Pa.

World wide sales through ALCOA INTERNATIONAL, INC., 230 Park Avenue, New York 17, N.Y.

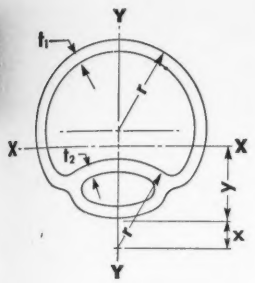


The development of DUOTRACE has opened broad new areas of design exploration in the field of heat transfer. By adding a second trace chamber to the one previously available in UNITRACE, DUOTRACE permits recirculation of the trace fluid. This opens up a whole new area of heat transfer design. Not the least of the possibilities is this: certain types of heat exchangers may now be extruded as single units. The cost savings implicit in such a unit are almost staggering. Alcoa engineers will be happy to assist you in exploring such design innovations in your own plant or process.

Fittings and connections for UNITRACE and DUOTRACE: Unflanged connections can be made easily and effectively with the special UNITRACE Trace Cap. As illustrated, trace chambers in adjoining sections are cut back and a circumferential weld is made to seal the product chamber. The cut back trace section is then covered with a UNITRACE Trace Cap welded in place with 4043 weld wire. Simple, efficient **flanged connections** utilize special UNITRACE flanges designed to accommodate both trace and product chambers. Jumper connections are used to carry the trace across the connection, and special impingement plates in the flange shield the product chamber from erosion as steam passes through the flange. **Valves, pumps and other fittings** can be incorporated into the traced systems by using UNITRACE flanges which mate with all 150-lb ASA flanges, valves and pumps. UNITRACE and DUOTRACE systems accommodate standard preformed pipe insulation.

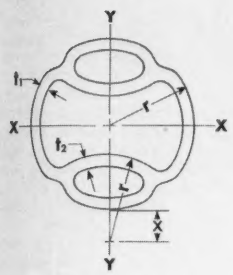


UNFLANGED CONNECTIONS FLANGED CONNECTIONS VALVES AND FITTINGS



	Unitrace Sizes	1 in.	1½ in.	2 in.	3 in.	4 in.	6 in.	8 in.
Axis XX	Moment of Inertia (I) in.⁴	.09	.34	.72	2.71	6.52	31.82	81.82
	Radius of Gyration (R) in.	.37	.58	.72	1.09	1.42	2.12	2.78
	Section Modulus (S) in.³	.13	.34	.56	1.42	2.65	8.73	17.22
Axis YY	Moment of Inertia (I) in.⁴	.09	.33	.70	2.65	6.36	29.72	76.70
	Radius of Gyration (R) in.	.37	.57	.71	1.08	1.40	2.05	2.69
	Section Modulus (S) in.³	.14	.34	.59	1.52	2.83	8.97	17.79

Sizes	1 in.	1½ in.	2 in.	3 in.	4 in.	6 in.	8 in.
r	.657	.950	1.187	1.750	2.250	3.312	4.312
t_1	.133	.145	.154	.170	.187	.280	.322
t_2	.145	.163	.174	.185	.200	.307	.354
x	.133	.344	.406	.625	.813	1.500	2.000
y	.61	.87	1.08	1.59	2.03	2.98	3.87



	Duotrace Sizes	1 in.	1½ in.	2 in.	3 in.	4 in.	6 in.	8 in.
Axis XX	Moment of Inertia (I) in.⁴	—	—	.80	3.06	7.53	—	—
	Radius of Gyration (R) in.	—	—	.74	1.12	1.46	—	—
	Section Modulus (S) in.³	—	—	.68	1.75	3.35	—	—
Axis YY	Moment of Inertia (I) in.⁴	—	—	.67	2.59	6.29	—	—
	Radius of Gyration (R) in.	—	—	.68	1.03	1.33	—	—
	Section Modulus (S) in.³	—	—	.57	1.48	2.80	—	—

Sizes	1 in.	1½ in.	2 in.	3 in.	4 in.	6 in.	8 in.
r	—	—	1.187	1.750	2.250	—	—
t_1	—	—	.154	.170	.187	—	—
t_2	—	—	.174	.185	.200	—	—
x	—	—	.531	.843	1.125	—	—
y	—	—	—	—	—	—	—

Unitrace-Duotrace Sizes	1 in.	1½ in.	2 in.		3 in.		4 in.		6 in.	8 in.
Product Area (in.²)	.64	1.68	2.72	2.36	6.38	5.67	10.84	9.74	24.64	42.79
Trace Area (in.² each)	.10	.16	.35	.22	.98	.61	1.86	1.07	2.85	5.12
Metal Area (in.²)	.65	1.03	1.39	1.46	2.28	2.46	3.24	3.53	7.05	10.60
Weight (lb/ft)	.77	1.22	1.66	1.72	2.71	2.89	3.85	4.16	8.38	12.60
*Min. Bend Radii (in.)	5	8	10½	10½	17	17	24	24	36	48
Wetted Perimeter (in.)										
Product	3.35	4.92	6.31	6.28	9.68	9.65	12.72	13.02	18.63	24.75
Trace (each)	1.49	1.71	2.40	1.87	4.13	3.22	5.32	4.23	6.75	9.63
Fitting Weights (lb)										
Trace-Caps	.102	.126	.240	.13	.464	.40	.674	.55	1.67	2.92
Elbows	.706	1.347	2.111	2.65	5.244	6.59	9.649	11.68	27.76	52.51
Impingement Plates	.024	.039	.057		.101		.162		.22	.34
Stub Ends				.65		1.50		2.13		
Terminal Casting				.50		1.12		1.75		

	1–2 in.	1½–2½ in.	2–3 in.	3–4 in.	4–6 in.	6–8 in.
Adapter Flanges	2.419	3.816	4.774	7.216	11.106	19.23

(Note: UNITRACE values are indicated in clear areas in the table above. DUOTRACE values are shown in the shaded areas.)
*Unitrace may be bent in any direction to these radii provided reasonable tooling is employed.

Aluminum Company of America, 875-J Alcoa Building, Pittsburgh 19, Pa.
Please send me the following literature covering Alcoa Aluminum for tubular products and other uses in the process industries:

☐ 10197 Aluminum Pipe and Fittings
☐ 10418 Alcoa Unitrace: Combines Piping and Tracing in One Unit
☐ 514 Alcoa Duotrace Technical Report
☐ 10270 Alcoa Utilitube
☐ 10460 Process Industries Applications of Alcoa Aluminum
☐ 11453 Solving Refinery Corrosion Problems with Aluminum
☐ 20849 Resistance of Aluminum Alloys to Weathering and Resistance of Aluminum Alloys to Chemically Contaminated Atmospheres
☐ 20437 Aluminum Alloy Heat Exchangers in the Process Industries
☐ 19416 Brazing Alcoa Aluminum
☐ 19415 Welding Alcoa Aluminum
☐ 19051 Alcoa Aluminum Handbook

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Title_____
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State_____

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ALUMINUM COMPANY OF AMERICA

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NEW PRODUCTS

(Continued From Page 48)

Chemical Co., 6216 West 66th Place, Chicago 38, Ill. The inhibitors described in the literature are designed for the following: protection of steam and condensate lines in boiler systems, method for treating and protecting recirculating water equipment and process water systems, how to treat water to insure trouble-free operation of cooling water systems and discussions on effects of galvanic corrosion in cooling systems.

Insulation

An insulation material useful to 2200 F and trademarked Tipersul has been developed by the Du Pont Company, Wilmington, Del. It offers low heat conductivity, ability to scatter infrared radiation and low density, thus making it useful for thermal, acoustical and electrical insulation, according to Du Pont. Tipersul may be added as filler to the fluorocarbon resins to increase dimensional stability of finished products.

•

Aluminum jacketing for protecting insulation on piping, tanks and towers is described in a bulletin available from Insul-Coustic Corp., 42-23 54th Road, Maspeth 78, N. Y. Photographs of typical installations are included.

Lubricants

An air drying solid film lubricant containing molybdenum disulfide has been developed by Hohman Plating & Mfg. Co., 814 Vermont Ave., Dayton 4, Ohio. Called Surf-Kote A-1290, it can be applied by spraying, dipping or brushing and is claimed to form a hard, durable film on most types of metal surfaces. It retains a low coefficient of friction over a range of pressures, temperatures and surface speeds to prevent galling, seizing, fretting corrosion, cold welding and similar friction problems, according to Hohman Plating. The company also claims Surf-Kote protects coated parts from corrosion when subjected to atmospheric conditions.

•

A high temperature lubricant claimed to have excellent thermal and oxidation-corrosion stability has been developed by Metal & Thermit Corporation, 100 Park Ave., New York, N. Y. Called Diphenylbis-n-Dodecylsilane, it is a colorless, mobile liquid designed to have good stability and temperature-viscosity ratio at high temperatures. According to the manufacturer, the lubricant exhibits no corrosive effects on metal parts in storage or when functioning.

Mergers

Assets of Allied Paint Manufacturing Co., Tulsa, Okla., have been acquired by the H. K. Porter Company, Inc., Pittsburgh 19, Pa. Allied will become the Tulsa Works of the Paint Division of Porter.

Non-Metallics

A castable mix of ceramic fibers and inorganic binder that is used directly from the shipping container is described in a new technical data sheet available from the Carborundum Company, Niagara Falls, N. Y. The mix is claimed to have a continuous use temperature range to 2300 F and shock resistance and will not be degraded by exposure to immediate rise from room temperature to 2100 F. Suggested uses are combustion chambers for industrial oil and gas fired furnaces, boiler access doors, metallurgical furnace covers, vessel linings and other furnace and oven wall applications.

•

Graphite woven fabrics and their relation to various industrial applications are given in a technical bulletin available from National Carbon Company, Division of Union Carbide Corp., 270 Park Ave., New York 17, N. Y. Chemical uses of the fabrics include filters, vapor condensers, catalyst carriers, mist eliminators, tower packing, cell diaphragms, anodes, cathodes and anode bags.

•

Plant floors can be protected from the destructive and costly effects of corrosion, according to descriptive literature available from the Ceilcote Company, 4832 Ridge Road, Cleveland 9, Ohio. In addition to pre-installation engineering of floors, the literature also recommends sealing of all vertical and horizontal areas with corrosion preventive materials to form a surface that will resist thermal shock, impact and spalling. Ceilcote's "Engineered Floors" are in service in the food processing, petroleum, paper and textile plants requiring protection from severe corrosive conditions, according to the company.

•

Laboratory table tops, sinks, hoods, shelves and other working surfaces subjected to physical and chemical abuse can be covered with a new monolithic asbestos-cement sheeting. Called Colorlith, the sheeting is described in a brochure available from Johns-Manville Corp., 22 East 40th St., New York 16, N. Y. The brochure gives tubular data on physical and chemical resistant properties of the sheeting and the thickness available.

Plastics

Savings to 60 percent in installation costs are claimed for a new line of rigid Kroseal vinyl electrical conduit available from the B. F. Goodrich Industrial Products Company, Akron, Ohio. Cost saving estimates are based on comparison with installation costs of metal or fiber conduit. The new conduit is recommended by the company for all types of electrical conduit systems and telephone circuits where unusual corrosive conditions exist. Koroseal conduit is fire resistant, self-extinguishing and will not support combustion, according to the manufacturer.

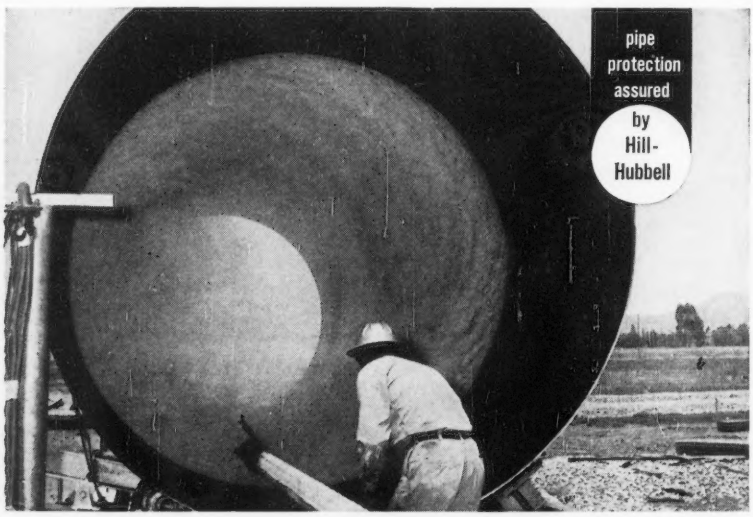
•

Extruded chlorinated polyether sheet in 48-inch wide rolls for lining tanks, vessels and other equipment is available from National Vulcanized Fibre Co., 1060 Beech St., Wilmington 99, Del. The material previously was available only in narrow widths. The wide rolls cut application costs by reducing the number of seams and welding time. Equipment lined with the plastic sheeting can be made of less expensive materials: For example, steel tanks can be fitted with the linings for protection against highly corrosive liquids.

•

A vinyl heat-reactive tubing which shrinks under heat provide a tight

(Continued on Page 54)



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For lifelong dependability in a vital power generating installation, these 13-foot diameter penstocks were lined, coated and wrapped by Hill-Hubbell corrosion protection experts.

Whether yours is a large or small diameter installation, the best possible protection you can specify is Hill-Hubbell, the name synonymous with quality in mill coated-and-wrapped pipe.

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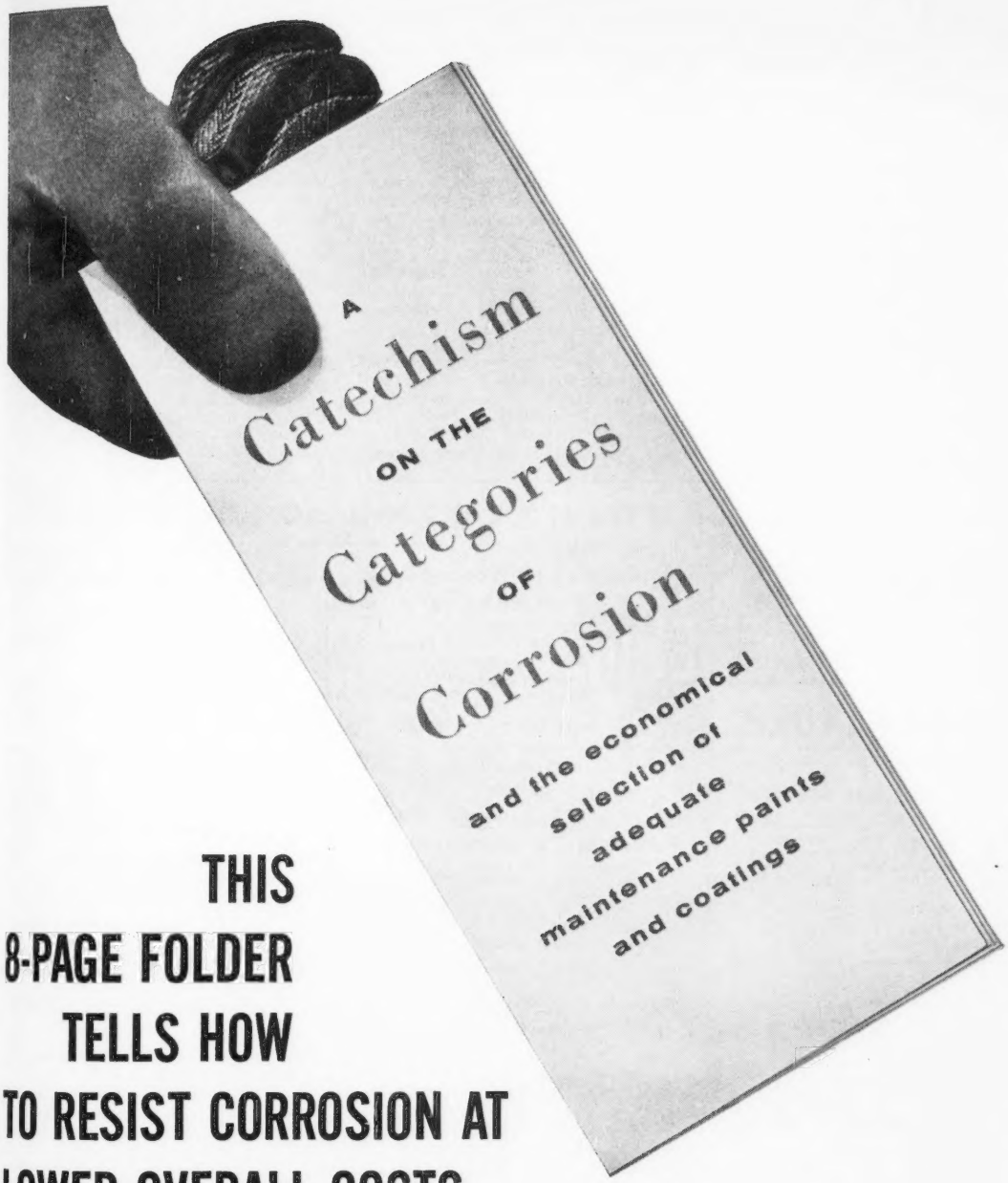

THIS 8-PAGE FOLDER TELLS HOW TO RESIST CORROSION AT LOWER OVERALL COSTS

If you have anything to do with maintenance of equipment or structure, or with the costs that result therefrom, this folder may be extremely useful to you. It gives a rational basis for paint and painting specifications, and tells how all surface and area exposures can be classified into the Four Categories of Corrosion.

As in all other phases of engineering, both underdesign and overdesign of maintenance painting carry economic penalties. Either one will show up sooner or later on the overall cost sheets. Although Hercules does not make any finished paints or coatings, we have had over twenty-five years' practical experience with Parlon® chlorinated rubber, a key material for corrosion-resistant and high-performance maintenance paints.

This booklet has been written with this background of experience. Write for your copy.

Cellulose Products Department

HERCULES POWDER COMPANY

INCORPORATED

900 Market Street, Wilmington 99, Delaware

CR 59-5

NEW PRODUCTS

(Continued From Page 52)

covering for symmetrical or gently contoured shapes is available as a clear, transparent tubing Minnesota Minning and Manufacturing Co., 900 Bush Ave., St. Paul 6, Minn. Designated as Scotch-Tite, the tubing is being used for covering harness cables, condensers, coils, ground straps, high voltage leads, bus bars and other items where a tight, abrasion and chemical resistant electrical insulating cover is required.

•

Fan housings, wheels and exposed parts of exhaust systems are being made of Heil Rigidon plastic for resistance to chemical fumes. The corrosion resistant fans have wheatherhoods for protecting motors and V-belt drives from weather exposure, according to the manufacturer, Heil Process Equipment Corp., 12850 Elmwood Ave., Cleveland 11, Ohio.

Rectifiers

Automatic control of potential current in cathodic protection systems has been developed by Electro Rust-Proofing Corp., 30 Main St., Belleville 9, N. J. Adaptable to present cathodic protection systems, the automatic control provides continuous indication of protective state of the structure, regulation of applied current, retarding of coating deterioration, conservation of power and anode material and prevents overload of the rectifier, according to the manufacturer.

•

One-unit cathodic protection rectifiers in four standardized case sizes are available from Eicor, a division of the Scranton Corp., 4059 West North Ave., Chicago 39, Ill., and 2225 Burbank, Dallas, Texas. Made of 11-gauge steel, the cases are designed to be small-arms proof. They can be pole or platform mounted, have wide swinging doors which can be padlocked and have Condulet fittings for input power connections. Eicor also designs and produces rectifiers to exact specifications as required by the engineer or customer.

Valves

Improvements have been incorporated in new models of the Massco-Grigsby pinch valve design to handle abrasive and corrosive pulps and liquids. Available with rubber or neoprene sleeves in sizes from 1 to 14 inches inside diameter and for pressures to 150 psi and temperatures to 200 F, the valves are manufactured by the Mine and Smelter Supply Co., 3800 Race St., Denver, Colo. The valves have a hydral-air operating mechanism designed to give easy, fast closing, and can be equipped for automatic regulation.

CORROSION ENGINEERING DIRECTORY

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Design and Installation of cathodic protection systems. Supervision. Resistivity and electrolysis surveys. Selection and application of protective coatings.
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Beat Corrosion with the different polyester...

ATLAC® 382

Lightweight, sturdy, reinforced plastic equipment —made with ATLAC 382 bis-phenol polyester resin—may offer an efficient, economical solution to your equipment corrosion problems. This unusual resin has maintenance applications, too: in glass reinforced tank linings and in "putty" materials for repairing cracks and holes in steel ducts and concrete floors.

ATLAC 382 is a special, bis-phenol polyester which almost universally retains a higher percent of original strength under corrosive conditions than general purpose polyester and isophthalic resins. See for yourself—write for our new comparative study* on the effects of corrosive chemicals on various resins.

*Presented before the Society of the Plastics Industry, Feb., 1960

Tub Liner Beats Corrosion

The Carl N. Beetle Plastics Corporation uses ATLAC 382 to fabricate corrosion resistant, seamless liners for steel tubs used to handle acids. Bonate® liners, made with ATLAC 382, extend the service life of the tubs several times beyond that which could be expected from steel alone, without a sign of deterioration by chemical attack. They're strong, lightweight, easily cleaned; surface stays free of pitting and contamination. (This application is just one of many in which the corrosion resistance of ATLAC 382 is effectively combined with the strength and economy of steel.)*

†Subsidiary of Crompton & Knowles Corporation

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ATLAS POWDER COMPANY
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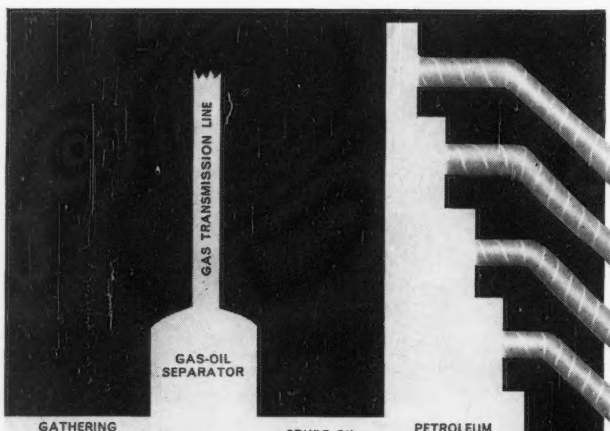
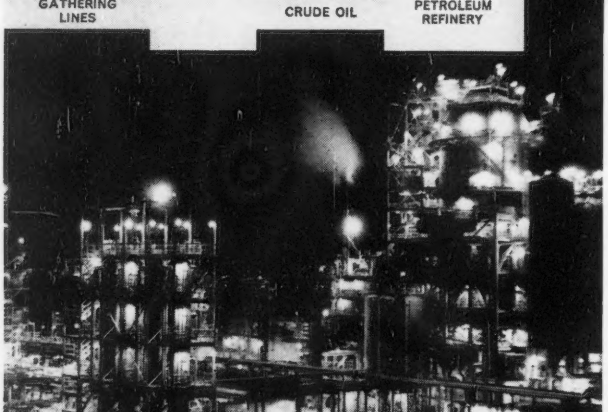
Polyken tape protects products lines

for this big Petro Company





Phillips pipe is cleaned and wrapped by Brodie Construction Company in a single factory-smooth operation. No primer, no drying or cooling. No fumes or fire hazards.

Another convinced user learns the money-saving versatility of one of the world's incredibly tough tapes

Phillips Petroleum Company chose Polyken No. 960 Extra-Strength Pipeline Tape to protect its products lines. This is why:

- Polyken 960 is a *dependable* pipeline coating. It is easy to handle, simple to apply, resulting in a reliable, quality installation.
- It is *especially* suited to construction of short lines and close work, as on these pipelines carrying crude oil fractions.
- It utilizes high-density polyethylene for maximum durability and corrosion resistance.
- It stands up under tough conditions of terrain and climate—experience-proved in many, many thousands of squares installed throughout the world, in plains, deserts, mountains, swamps.
- Its cathodic protection requirements are low.

AND . . .

- It saves money: Polyken 960 goes on fast with less men per job, covers more miles per day. Less equipment, less handling costs. More savings over the old hot dope idea.

See your Polyken Man . . . call your Polyken Tape Coating Distributor . . . or write Polyken, 309 West Jackson Blvd., Chicago 6, Illinois.

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Incandescent Supply Co.

San Francisco, Calif.
Phillips & Edwards Electric Co.

Seattle, Washington
Farwest Corrosion Control Corp.

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Pacific Water Works Supply Co.

St. Louis, Missouri
Shutt Process Equipment Co.

Tulsa, Oklahoma
Midwestern Pipe Line Products Co.

Polyken

Experienced in modern PROTECTIVE COATINGS

MEN in the NEWS

Glen H. Tanner, Jr., has been appointed technical consultant for Pipe Inspectors of Lafayette, La., a division of Plastic Applicators, Inc., Houston, Texas.

•

John M. French has joined Pennsalt Chemical Corporation, Natrona, Pa., as manager of development for the company's Corrosion Engineering Products Department.

•

A. J. Teller has been appointed technical director at Colonial Iron Works Co., Cleveland 10, Ohio.

•

Angus Scott is silicon products sales manager for International Rectifier Corp., El Segundo, Cal.

•

John G. Gill has been appointed assistant director of process development in Crucible Steel Company's Technology Department, Pittsburgh 22, Pa.

•

Robert C. Schroeder has been appointed manager of film and sheeting for Union Carbide Plastics Company, 30 East 42nd St., New York 17, N. Y.

•

Vernon W. Schroeder has been promoted to development associate in the Development Department of the company's plant at Bound Brook, N. J.

•

NACE Corporate Representative recently appointed for Humble Pipe Line Company, Houston, Texas, is **P. D. Phillips, Jr.,** vice president of planning and economics. He replaces **A. E. Pecore,** who has retired from Humble.

•

Two new members elected to the board of directors for Hagan Chemicals & Controls, Inc., Pittsburgh 30, Pa., are **C. L. Barksdale,** vice president of jobber sales division, and **T. W. Bruner,** president of Bruner Corporation, Milwaukee, Wis.

•

Fred A. Compton has been appointed a director of the Hinchman Corp., Francis Palms Bldg., Detroit 1, Mich. **Edward T. Vincent** has been appointed an associate and consultant for the company.

•

Antoine Marc Gaudin has been elected as chairman of the Engineering Foundation of the United Engineering Trustees, Inc., 29 West 39th St., New York 18, N. Y.

•

Lewis M. Duckor has been appointed vice president of engineering for Colvin Laboratories, Inc., 364 Glenwood Ave., East Orange, N. J.

•

Howard L. Gerhart is director of Pittsburgh Plate Glass Company's Springdale Research Center.

•

A. James Kiesler of the General Electric Research Laboratory, Schenectady, N. Y., has been awarded the honorary professional degree of Metallurgical Engineer by the University of Missouri School of Mines and Metallurgy.

•

Clarence H. Linder has been elected president of the American Institute of Electrical Engineers. He is a vice president of General Electric's Electric Utility Group.

•

T. G. Lipscomb II has been promoted to senior research chemical engineer in Humble Oil & Refining Company's Research and Development Division at Baytown, Texas.

•

Robert A. Weaver, Jr., has been named to the newly created position of board chairman for the Bettinger Corporation, Milford, Mass. **J. H. Kent Lyons** was named president and director.

•

A. H. McArn has joined the engineering service department of A. M. Byers Company, Clark Bldg., Pittsburgh, Pa.

•

Johnstone S. Mackay has been named director of the research and development department of Pittsburgh Chemical Company, Porter Bldg., Pittsburgh 19, Pa.

•

Henry Petronis has been elected vice president of manufacturing for Pall Corporation, Glen Cove, N. Y.

•

Fred L. Plummer has been elected vice president of the International Institute of Welding. He is national secretary of the American Welding Society.

•

NACE member **Robert C. Putnam** has been appointed chief chemist for the United States Testing Company, Inc., 1415 Park Ave., Hoboken, N. J.

•

John T. Lurcott has been appointed territorial sales manager of the metropolitan New York area for the Alloy Tube Division of Carpenter Steel Co., Union, N. J.

•

NACE Member **Herman S. Preiser** has been promoted to assistant project manager and associate consultant of the Advance Concepts Section of the Electrical-Electronic Design Branch of the Bureau of Ships.

•

Clifford J. Grube has been appointed manager of field sales for the Metals and Controls Division of Texas Instruments, Inc., 34 Forest St., Attleboro, Mass.

•

Ben Allen is the new director of engineering at Corning Glass Works, Corning, N. Y.

•

Robert S. Baker has been appointed vice president of manufacturing for the American Brass Company, a subsidiary of the Anaconda Company, 25 Broadway, New York 4, N. Y.

•

Vincent J. Coppola, a new NACE member, has formed the firm Metallurgical Consultants at 2100 Quitman, Houston, Texas. The firm will provide services on heat treating, material selection, machining, failure analysis, corrosion, joining methods and ferrous and non-ferrous alloys.

•

George L. Bedford is the new territorial manager in the Los Angeles area for Carpenter Steel Company's Alloy Tube Division. Offices will be at 2304 Huntington Drive, San Marino, Cal.

•

Persa R. Bell, co-director of the Thermonuclear Experimental Division at

(Continued on Page 58)

MEN in the NEWS

(Continued From Page 57)

Oak Ridge National Laboratory, Oak Ridge, Tenn., is one of five U. S. nuclear scientists now visiting the Soviet Union for the second exchange of visits by technical teams between the two countries.

•

John S. Billingsley, assistant to the vice president of sales for Crucible Steel Company, Pittsburgh 22, Pa., has retired after 37 years of service.

•

William Bobrick and **Louis Maier** are recent appointments to the engineering-chemical department of Pittsburgh Chemical Company, Grant Bldg., Pittsburgh 19, Pa.

•

W. B. Brown has been named sales manager of the products branch of the Dow Industrial Service Division of the Dow Chemical Company, Midland, Mich.

•

T. Maurice Butler, George B. Holmes and **Brian W. Pollard** have been appointed assistant to the vice president of manufacturing and engineering of Burroughs Corporation, Detroit 32, Mich.

•

Richard G. Caulton has been appointed eastern sales manager for Apex Smelting Company at the Cleveland, Ohio, plant.

•

NACE Member **John B. Cruell** has been promoted to manager of the southern California district of Nalco Chemical Company's Industrial Division with headquarters in Glendale, Cal.

•

John C. Douglas has been appointed vice president of operations and **David Swan** vice president of technology for Union Carbide Metals Company, a division of Union Carbide Corp., 270 Park Ave., New York 17, N. Y.

•

Andrew Dravnieks, an NACE member, has been named scientific advisor in chemistry research at Armour Research Foundation of the Illinois Institute of Technology, 35 West 33rd St., Chicago 16, Ill.

•

Charles L. Faust, chief of the electrochemical division at Battelle Memorial Institute, Columbus, Ohio, has been awarded the American Electroplaters' Society's Scientific Achievement Award.

•

Noah E. Hull, vice president and general manager of Hughes Gun Company, Houston, Texas, has been elected president of the National Society of Professional Engineers.

•

Peter G. Kenedi has been appointed laboratory supervisor for Metal & Thermit Corporation's Research Laboratories in Rahway, N. J.

•

A. N. Voripaieff has been appointed New York division manager for A. M. Byers Company, Clark Bldg., Pittsburgh, Pa. He succeeds **Victor C. Lawrence,** who has been appointed Byers' general manager of sales.

•

NACE Member **Henry B. Linford,** professor of chemical engineering at Columbia University, New York, N. Y., has been awarded the Edward Goodrich Acheson Gold Medal and $1000 Prize by the Electrochemical Society, Inc.

•

Donald A. M. Mackay has been appointed director of research at Evans Research and Development Corp., 250 East 43rd St., New York 17, N. Y.

•

Charles H. Moore has been appointed technical director of the Copper Products Development Association, Inc., 50 West Gay St., Columbus 15, Ohio.

•

NACE Member **E. E. Nelson** has been transferred by his company, Socony Mobil Oil Company, Inc., to its Corrosion and Metallurgy Group, Research Department, Paulsboro, N. J.

•

Fritz Nussbaum has been advanced to executive vice president in charge of operations at Apex Smelting Company, 2537 West Taylor St., Chicago 12, Ill.

•

Paul E. Paules has been appointed western regional manager for the Scientific and Process Instruments Division of Meckman Instruments, Inc., 2500 Fullerton Road, Fullerton, Cal.

•

Robert I. Peters has been named manager of the Rigidon plant of Heil Process Equipment Corporation, 12901 Elmwood Ave., Cleveland 11, Ohio.

•

Robert W. Reinicke has been named vice president of operations for Ansul Chemical Co., Marinette, Wis.

In production of high-purity thorium...

Nickel resists attack by chlorine and its compounds at 400° C

When you start with crude thorium tetrachloride, it takes a little doing to wind up with a high quality thorium metal.

That's because crude thorium tet is full of impurities, metallic chlorides HCl and Cl_2. Getting rid of these "unwanteds" poses something of a problem.

Here's how the U. S. Bureau of Mines does it. The thorium tet is first volatilized at 800°C, then condensed at 400°C. Nickel is used as the condenser material because of its outstanding resistance to attack by hot metallic chlorides, HCl and Cl_2.

In 16 to 20 hours, a 10-kilogram batch of thorium tet is completely volatilized. After cooling, the nickel condenser is removed from the furnace. One end is placed in a plastic bag filled with argon, and is rapped with a mallet to dislodge the crystalline tetrachloride. Thorium tet is later reduced with sodium to yield the high-purity metal.

Nickel offers many advantages for handling chlorine and chlorine compounds. It displays excellent resistance to acid, alkaline and neutral chlorides. It resists corrosive attack, pitting and stress-corrosion cracking in chloride solutions, stands up under applied stress, alternate wetting and drying, vapor phase exposure, and even drastic conditions of temperature, agitation and aeration.

Low maintenance, too. Because of its high resistance to destructive conditions, nickel equipment usually requires only a minimum of maintenance attention. Its use puts you in line to attain some long-range economies.

And good workability. Nickel is readily formed and welded. Welded seams are just as strong and corrosion-resisting as the metal itself, and require no heat treatment after fabrication to produce maximum properties.

For further information on the uses of Nickel for handling chlorine and chlorine compounds — or for help in selecting materials to meet a specific need — write us.

HUNTINGTON ALLOY PRODUCTS DIVISION
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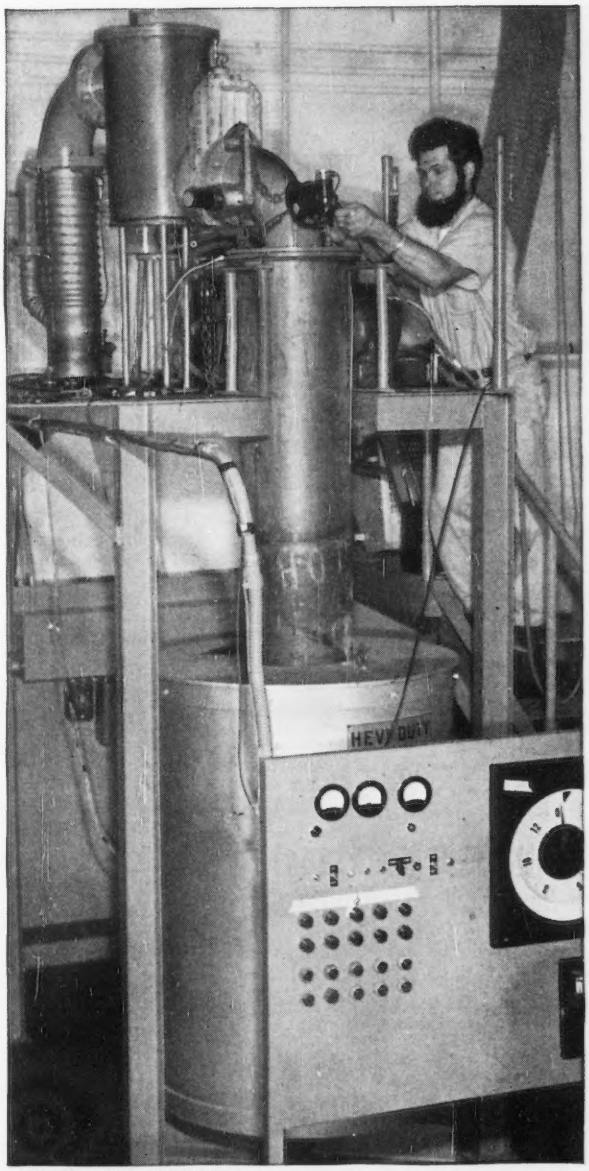
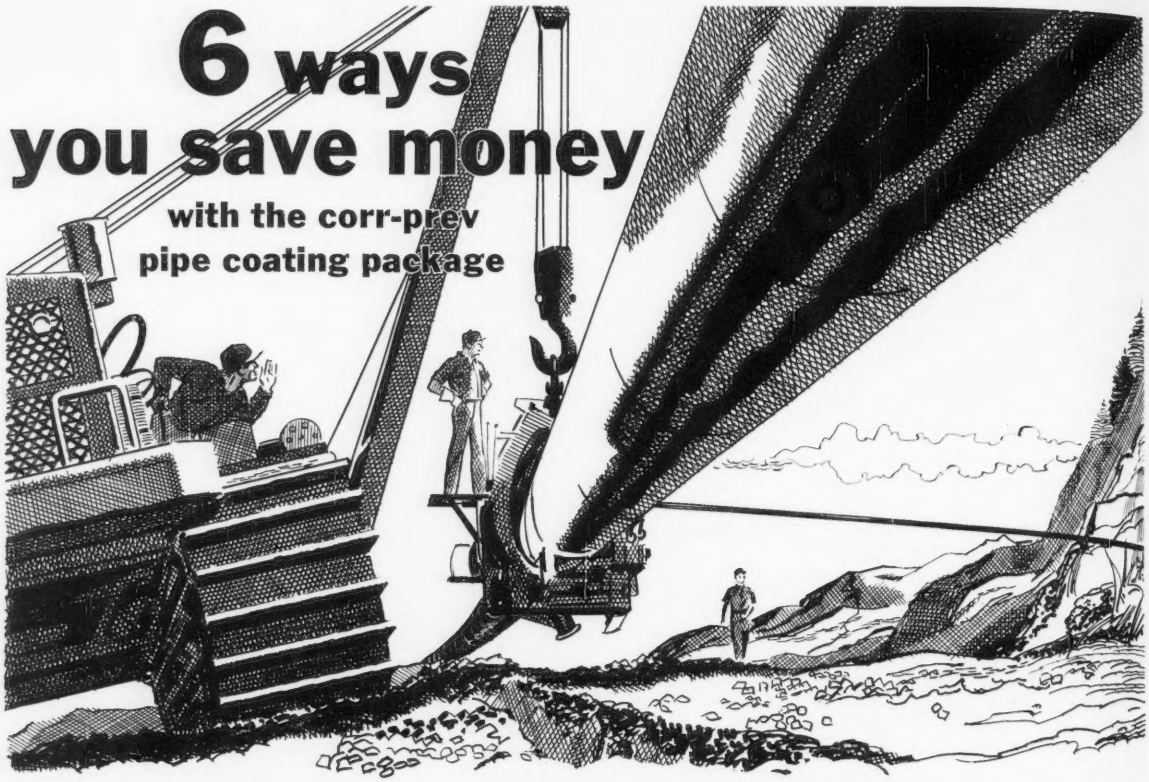


PURIFICATION FURNACE. Impurities are removed from crude thorium tetrachloride by high-temperature vacuum distillation carried out in a retort. The retort is fitted with a nickel condenser. Nickel was selected because of its resistance to metallic chlorides, chlorine and hydrogen chloride. *Photo courtesy U.S. Bureau of Mines, Albany, Ore.*

NICKEL

6 ways you save money

with the corr-prev pipe coating package



1 EASIER, CLEANER APPLICATION... no primer, no hot dope messes, no waste material.

2 LOWER LABOR COSTS... smaller, faster-moving wrapping crews.

3 HIGH-SPEED MACHINERY... power-wrapping equipment available from low-coast rental pools.

4 COMPLETE COATING PACKAGE... one-source package includes **all** items for coating construction.

5 CONSISTENT QUALITY... factory-uniform thickness and quality not found with field applied hotcoats.

6 LONGER LASTING PROTECTION... positive corrosion prevention, plus low cathodic protection costs.

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Polyethylene Pressure-Sensitive Protective Tape Coatings.

Chasewrap*
Abrasion-Resistant, Wrinkle-Free Overwrap.

Chaseprime*
Liquid Adhesive Primer.

Chasefil*
Putty Type Filler Material.

*Trade name of Chase & Sons, Inc., long-famous for protective and insulating tapes for electrical wire and cable.

How much can you *save* by protecting your piping installations with the new CORR-PREV Pipe Coating Package? First of all, you save pipe . . . because CHASEKOTE tape offers all the proven corrosion-resistant advantages of *polyethylene* tape. There are extra savings, too, in materials handling and storage. Savings in labor and coating application. Minimum pipe maintenance and reconditioning. Far less cathodic protection current demand. And a lot more!

Compare actual savings for yourself. Write for samples of CHASEKOTE and CHASEWRAP . . . and a *cost-per-foot* estimate to put the new CORR-PREV Pipe Coating Package to work on your next job. It'll save you money.

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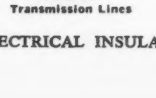
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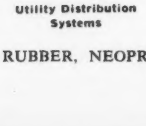
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Twenty-Five Committee Meetings Are Scheduled

Regional Conference Sessions to Discuss Diverse Problems

Corrosion problems covering the diverse fields from oil and gas well equipment, pipe lines and protective coatings to the process and refining industries will be discussed during the 25 NACE technical practices committee meetings scheduled at the regional conferences next month.

The committee meetings have been scheduled for the Northeast Region Conference (October 11-14, Prichard Hotel, Huntington, W. Va.), the North Central Region Conference (October 19-20, Pfister Hotel, Milwaukee, Wis.) and the South Central Region Conference (October 25-27, Mayo Hotel, Tulsa, Okla.)

South Central Region Conference

A total of 15 committee meetings is set for the South Central Region Conference in Tulsa, Okla. These will include discussions of oil and gas well equipment, pipe line corrosion, protective coatings and refining industry corrosion.

The following unit committees of Group Committee T-1 (Corrosion in Oil and Gas Well Equipment) are scheduled in Tulsa: T-1C, T-1D, T-1F, T-1G, T-1H and T-1E.

Unit Committee T-2 (Pipe Line Corrosion) will meet during the South Central Region Conference. The following unit committees of T-2 also will meet: T-2K, T-2D and T-2B.

Three unit committees of T-6 (Protective Coatings) have scheduled meetings in Tulsa: T-6B, T-6D and T-6E.

Group Committee T-8 (Refining Industry Corrosion) and its Task Group Committee T-8A (Chemical Cleaning) have planned meetings for the Tulsa Conference.

North Central Region Conference

Only one technical committee meeting has been scheduled for the October 19-20 North Central Region Conference: Task Group T-5C-2 (Corrosion by Cooling Waters—North Central Region).

Northeast Region Conference

The nine technical committee meetings scheduled during the Northeast Region Conference will be concerned with general corrosion problems, pipe line corrosion, corrosion problems in the process industies, protective coatings and corrosion coordinating committee activities.

The following committees have set meetings for the October 11-14 Conference in West Virginia: T-2K, T-5A, T-5E, T-6A-12, T-7A, T-6A, T-6F and T-6A-17.

Fifty-Three Attend Dallas Meeting of T-2C Committee

A total of 53 members and guests participated in the discussions held during the Dallas meeting of Unit Committee T-2C (Criteria for Cathodic Protection).

Discussions included report on work done to determine the relationship between cathode potential and protection from corrosion as it was related to cathodic protection of iron materials in water environment.

T-8A Elects New Officers

New officers elected for Unit Committee T-8A (Corrosion Occurring During Chemical Cleaning) are Chairman K. R. Walston of Standard Oil of Indiana, Whiting Ind., Vice Chairman C. M. Loucks of Sinclair Refining Co., Westlake, Ohio, and Secretary R. L. Hildebrand of Harvey, Ill.

Membership in NACE Technical Unit Committees

A question frequently asked by guests attending meetings of Technical Unit Committees is "How may I become a member of this committee?" This question is answered in the following procedure quoted from the Technical Committee Operation Manual:

1. Any member of NACE (irrespective of place or country of residence) may become a member of a Technical Unit Committee upon fulfillment of the following requirements.

2. He should apply in writing to the Chairman of the Unit in which he desires membership, stating his interest and willingness to participate in the activities of the Unit and giving his experience in the subject.

3. Approval by the Chairman of the Unit Committee of the application or by majority vote of committee members by letter ballot is necessary for appointment of an applicant to membership in a Unit Committee.

4. The Chairman of the Unit Committee will notify each applicant of his acceptance or rejection.

A directory of NACE Technical Unit Committees and Officers is published in the January, April, July and October issue of CORROSION.

Three Reorganized T-5A Task Groups Report on Meetings

The three reorganized task groups under Unit Committee T-5A (Corrosion in the Chemical Industry) held meetings during the Dallas Conference. At a joint meeting of Committee T-5A, plans were made for a meeting to be held during the Northeast Region Conference (October 11-14, Huntington, W. Va.).

The three T-5A task groups are as follows: T-5A-1 (Inorganic Acids and Derivatives), T-5A-2 (Organic Acids and Derivatives) and T-5A-3 (Alkali Enrivonments).

The chairman of T-5A-1 explained to the members that specific corrosion problems will be discussed at meetings and then re-considered at later meetings for further information and to clarify problems brought up.

At the T-5A-2 meeting, discussions were held on corrosion problems related to formic, acetic and benzoic acid in services with several metals. The committee also asked for laboratory and field corrosion data and experience in the following areas:

(1) Effect of chloride contamination from 10 to 10,000 ppm on corrosion of austenitic stainless steels, copper and copper alloys and Hastelloy C in acetic acid environments, (2) Effect of formic acid, butyric acid and propionic acid contamination of acetic acid solutions on corrosion resistance of common materials of construction, (3) Service experience with plastic piping in acetic acid service and (4) Service experience with low carbon grades of as-welded 304, 316, 317 and 319 grades of stainless steel for pipe and tubing in acetic acid service.

Discussions at the T-5A-3 meeting were on four general topics of alkali corrosion: (1) stress corrosion cracking in caustic soda, (2) general corrosion in caustic solutions at high temperatures, (3) corrosion in ammonia environments and (4) corrosion in amine solutions.

Other problems discussed included upper stress limits needed, use of coatings to prevent stress corrosion cracking, effects of chlorides and sulfides and the susceptibility of cast iron to stress corrosion cracking.

T-3G Discusses Pilings

A general discussion on cathodic protection of steel pilings was held during the Dallas meeting of Unit Committee T-3G (Cathodic Protection). Information on the effect of water velocity on cathodic protection requirements and corrosion of a wharf in Sumatra was presented by a member. This included economic data that showed replacement cost per piling was $750 while only $100 per piling for cathodic protection for 10 years.

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McCormick Is Elected New T-4B Committee Chairman

L. O. McCormick of the Baltimore Gas and Electric Co., Baltimore, Md., has been elected chairman of Technical Committee T-4B (Corrosion of Lead and Other Metallic Cable Sheaths).

A member of NACE since 1947, he has been affiliated with the Baltimore utility company since 1927. Since 1943, his work has been on cable line corrosion problems. He has been active in NACE technical committee work and has been a member of Committees T-4B and T-4C since their formation. He also has served as co-chairman of the Electrical and Communications Symposium at the 1954 NACE Annual Conference.

McCormick

Task Group T-5C-1 Holds May Meeting in Houston

Thirty-six members and guests attended the May 20th meeting in Houston of Task Group T-5C-1 (Corrosion by Cooling Water—South Central Region). After a talk on pretreatment of cooling water equipment, a discussion was held on a variety of topics including the following: recommended procedures for pretreating bundles, use of a meter to determine cooling water corrosion and the fouling of heat exchanger equipment.

Other discussion topics were service life of steel equipment in cooling water, non-ferrous and high alloy equipment service life in cooling water, wood deterioration in cooling towers, side stream filters and the advantages of filtration for improving heat transfer and performance of cooling water inhibitors.

Dezincification Paper Given at T-4F-1 Meeting

A paper on dezincification and a discussion on cavitation, erosion and corrosion were included in the meeting of Task Group T-4F-1 (Materials Selection for Corrosion Mitigation in the Water Industry) held during the NACE Dallas Conference last March.

The paper on dezincification presented by T-4F-1 Chairman Daniel Cushing included slides showing different types of corrosion by case histories and a series of ancient bronzes showing formation of films over a long period.

T-6J Meeting at Dallas

Publication of color plates on standards for sandblasting cleanliness was discussed by Technical Unit Committee T-6J (Los Angeles Area, Protective Coating Application Problems) at its Dallas meeting in March. This work is a project of the committee's Task Group T-6J-3 (Inspection Techniques).

Appliance Corrosion May Be Considered by T-4E

Unit Committee T-4E considered expanding its scope to include the corrosion of household appliances at its meeting last March during the Dallas Conference.

A Survey is being made of suppliers in the appliance industry to determine if there is sufficient interest and if active cooperation from industry can be expected. If favorable reports are received from the survey, T-4E will consider forming a task group to study such problems as water corrosion problems in the use of driers, refrigeratos, heaters, washers, etc.

The committee decided to continue its exposure tests of various pipe metal samples in domestic waters throughout the U.S. and Canada.

Ontario Electrolysis Group Celebrates 10th Birthday

The Southern Ontario Committee on Electrolysis, which is affiliated with Committee T-7F (Canadian Region Corrosion Coordinating Committee), held its 10th Anniversary general committee meeting and luncheon on June 9. The meeting included election of officers, a guest speaker, a film on zinc and a round table corrosion panel.

Officers elected were Chairman L. F. Heverly, Trans-Canada Pipe Line Ltd., Vice Chairman D. W. Lemon, Imperial Oil Limited, and Secretary-Treasurer R. C. Campbell, United Gas Limited.

Guest speaker H. J. Hartman's topic was a review of experiences with stray current corrosion problems.

T-6B Meetings

A total of 68 guests and members attended the Unit Committee T-6B (Protective Coatings for Resistance to Atmospheric Corrosion) meeting held during the Dallas Conference. Reports from seven task groups were given.

T-6B has scheduled a meeting next month at the South Central Region Conference (October 25-27) in Tulsa, Okla.

A discussion was held at the Dallas meeting on how the committee work could be done faster.

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Over 20 million dollars was paid in 1959 to 39,000 employees of one company through the company's savings plan.

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Northeast Region's 1960 Conference will be October 11-14 at the Prichard Hotel, Huntington, W. Va.

Nace Technical Reports

STRESS CORROSION CRACKING. 15 papers reprinted from Corrosion. Pub. 59-4. Postpaid, per copy $5

HIGH PURITY WATER CORROSION. Sixteen papers reprinted from Corrosion. Pub. 59-3. Postpaid, per copy $3

1957-58 NACE TECHNICAL REPORTS. 38 reports reprinted from Corrosion. Includes some in Pub. 59-2 and 3 above. Postpaid, per copy. $6.50

Remittances must accompany all orders for literature the aggregate cost of which is less than $5. Orders of value greater than $5 will be invoiced if requested. Send orders to National Association of Corrosion Engineers, 1061 M & M Bldg., Houston, Texas. Add 65c per package to the prices given above for Book Post Registry to all addresses outside the United States, Canada and Mexico.

Technical Program Changes Are Given for Regional Conferences

Final changes in the technical programs of five NACE regional conferences are given below under each region's heading. A diversity of corrosion problems will be discussed on the programs as related to specific industries in the various regional areas. General corrosion control methods also will be covered such as protective coatings, inhibitors and cathodic protection.

News items pertaining to the regions also are given under each of the regional sub-headings.

Southeast Region Conference
October 6-8
Dinkler-Plaza Hotel
Atlanta, Georgia

Registration fee will be ten dollars for members and non-members attending the October 6-8 Southeast Region Conference in Atlanta.

Two papers have been added to the list which was published on Page 62 of the June issue of CORROSION Magazine: Corrosion Problems in Kraft Pulp and Paper Mills—1960 Answers by David F. Roberts of St. Regis Paper Co., Jacksonville, Fla., and Recent Commercial Developments in Corrosion Resistant Metals by Carroll L. Wagner of J. M. Tull Metal & Supply Co., Inc., Atlanta.

Two films also have been added to the program: one on surface preparation by sandblasting and one entitled "Voices Under the Sea."

Special events scheduled for the conference include a banquet, the football game between Georgia Tech and LSU and a ladies' program including a sightseeing trip through Atlanta's famous points of interest such as the residential area, Stone Mountain, Cyclorama, home of Joel Chandler Harris Kennesaw Mountain National Park, etc.

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Wilmington Section has scheduled a dinner meeting for September 28 at Fabian's Restaurant in Claymont, Del. Speaker will be B. S. Payne of Pfaudler Permutit, Inc., whose topic will be use of zirconium, titanium and tantalum in the chemical industry.

Northeast Region Conference
October 11-14
Prichard Hotel
Huntington, West Virginia

The changes and additions to the Northeast Region Conference program and abstracts of papers printed on Pages 48 and 49 of the August issue of CORROSION Magazine are given below.

Two papers have been added to the Inhibitor Symposium: Use of Inhibitors in Commercial Cleaning Operations, by Grover Mullin, Dow Chemical Co., Cleveland, Ohio and Use of Inhibitors in Refinery Corrosion Problems, by R. B. Thompson, Universal Oil Products Co., Des Plaines, Ill.

In the High Temperature Corrosion Symposium, E. N. Skinner will be a co-author with J. J. Moran and J. K. Mihalisin.

Two papers have been added to the Fresh Water Corrosion Symposium: Recirculated Cooling Systems, by J. M. Brooke, Phillips Petroleum Co., Sweeny, Texas, and Principles of Water Treatment, by K. C. Channabasappa, Wright Chemical Co., Chicago. Ill.

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Baltimore - Washington Section has scheduled five of its future programs as following: September 20, Navy Tank Coating Program by L. S. Birnbaum; November 15, slide talk on 1960 national meeting by C. A. Muller; February 21, corrosion problems in water handling by D. W. Auld; and April 18, characteristics of hot dip galvanized coating by H. R. Breslau.

North Central Region Conference
October 19-20
Pfister Hotel
Milwaukee, Wisconsin

The only change in the technical program for the North Central Region Conference as published on Pages 58 and 59 of the August issue of CORROSION Magazine is the addition of one technical paper to the Brewing Industries Symposium schedule for Wednesday afternoon, October 9. The paper recently added is entitled "Effect of Metal Ions in the Food and Beverage Industry" by Fred Fink and John Litchfield, Battelle Memorial Institute, Columbus, Ohio.

Part of the entertainment for the conference will be a social hour set for Wednesday evening, October 9.

Registration fee for the conference will be twelve dollars which will cover attendance of all technical and committee meetings, the luncheon-business meeting and social activities.

•

Chicago Section has scheduled the following topics for its meetings through May, 1961:

September 20: Ladies Night.

November 15: Tape Coating Forum and Panel, moderated by Ralph Bowers of Industrial Coatings Co.

January 17: Engineering Cathodic Protection Systems for Communication Cables, by T. J. Maitland, American Telephone and Telegraph Co.

February 21: Past Chairman's Night, moderated by Wayne Schultz, Dearborn Chemical Co.

March 21: Corrosion Contractors Panel.

April 18: Corrosion Problems in Nuclear Reactors, by Sherman Greenberg of Argonne National Laboratory.

May 16: New Coating Resins to Combat Corrosion.

South Central Region Conference
October 25-27
Mayo Hotel
Tulsa, Oklahoma

Scheduling of the six technical symposia for the South Central Region Conference has been set as follows:

October 25: the Oil and Gas Pipeline Symposium will be held during the morning; the Oil and Gas Production Symposium in the afternoon.

October 26: Chemical Processing and Refining, morning; Protective Coatings and Plastics, afternoon.

October 27: Water Handling Symposium in the morning; Corrosion Survey and Testing in the afternoon.

Fifteen NACE technical committee meetings are scheduled during the conference and will be held concurrently with the symposia.

A business luncheon with guest speaker and a banquet are set for Wednesday, October 26 with a fellowship hour on Tuesday night. An entertainment program for the ladies also has been planned.

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Alamo Section members have selected the Granada Hotel in San Antonio as the headquarters for the 1962 South Central Regional Conference.

At its August 16 meeting, the section held a discussion on a technical article recently published in CORROSION. Discussion leader was Max Schlather of United Gas Pipe Line Co.

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Houston Section heard Jack L. Battle of Humble Oil & Refining Company give a review of the current state of cathodic protection practices in well casing at the August 9 meeting.

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North Texas Section has scheduled the following programs for its future meetings:

September 12: Aluminum for Corrosion Control Applications, by M. E. Carlisle of Aluminum Company of America.

October 10: Cathodic Protection Studies Lab and Field, by A. R. Erben of the Sun Oil Company.

November 14: New Techniques of Inhibition in Producing Oil and Gas Wells, by D. R. Fincher of Tidewater Oil Company.

Western Region Conference
October 6-7
Sheraton-Palace Hotel
San Francisco, California

No changes have been made in the technical program for the Western Region Conference as published on Pages 52 and 53 of the August issue of CORROSION Magazine.

Two luncheons for the Western Region officers have been scheduled for October 6 and 7. A hospitality hour is set for Thursday evening, October 6, with a banquet following.

SEE Page 61 for information on NACE Technical Committee meetings scheduled at the regional conferences.

AMCHEM Information Bulletin

Facts about pickling acid inhibitors

Nearly 40 years ago Amchem developed the first pickling acid inhibitor—RODINE—and with it revolutionized acid pickling. Only a few of the steel mills of the time believed that the addition of less than one percent RODINE to a sulfuric acid pickling bath could save substantial amounts of acid and metal, while increasing the life of the bath. Today there is no mill chemist who does not know about RODINE and its proven performance in eliminating waste of valuable metal and acid, and its ability to pay for itself through the savings thus gained.

In the past few years much attention has been focused on the use of wetting agents to accelerate pickling. But the fact remains that pickling cycles cannot be reduced by the use of wetting agents alone without severe overpickling problems. Wetting agents do help the acid run off surfaces removed from pickle baths, and, in so doing, reduce carry-over of acid into the rinse.

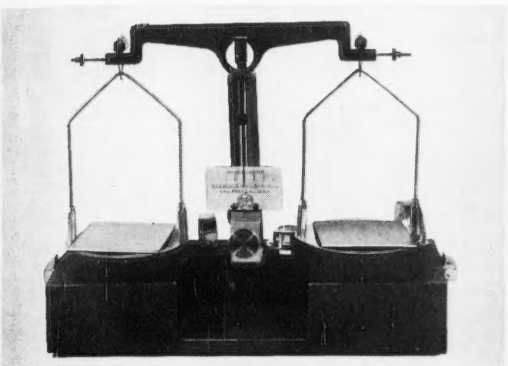
Wetting agents should not be confused with inhibitors to protect the metal and save acid wasted in pitting it. They should not be expected to miraculously speed the removal of scale, even at the expense of wasting the metal. However, the *proper* combination of *real inhibitor* plus correct wetting agent can have beneficial effects on pickling practices.

Only a true inhibitor such as RODINE can offer steel producers solid advantages in pickling. Baths can be operated longer and less acid is required to keep them at desired concentration. Costs of charging and cleaning the bath are reduced, less handling and storing of acid is required. A RODINE bath produces far fewer rejects—steel emerges with uniformly smooth, bright clean surfaces, free of pits, blisters and smut.

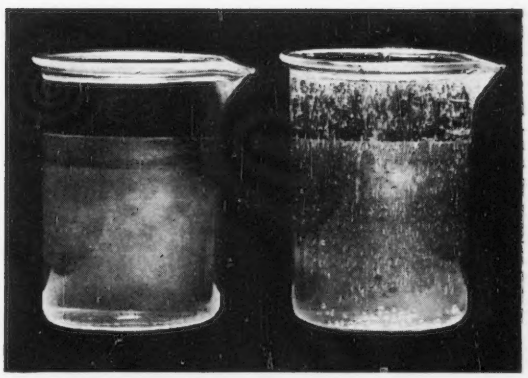
When an Amchem Technical Representative enters your pickle house, you can be assured of experienced assistance in improving your pickling. He will recommend the proper RODINE to 1) prevent needless consumption of acid after scale removal, 2) prevent smutting, pitting and overpickling, 3) produce a stable, free-rinsing foam blanket, 4) improve rinsability and reduce carry-over, and 5) produce a brighter, cleaner surface. Only the Amchem Representative can do this for you because he has at his command the most widely diversified and accepted line of real inhibitors and correct wetting agents available.

Since the early days of pickling acid inhibitor development, scientists in the Amchem Metal Protection Laboratories have constantly studied methods to make the RODINES stronger, more effective and more economical to use. The RODINES of today, as of 40 years ago, are in a class by themselves, have developed a reputation as *the international standard* in acid pickling inhibitors. The fruit of these years of laboratory research and experience in a highly specialized field, and the assistance of Amchem's trained field representatives—specialists in acid pickling techniques—are at your disposal for the asking.

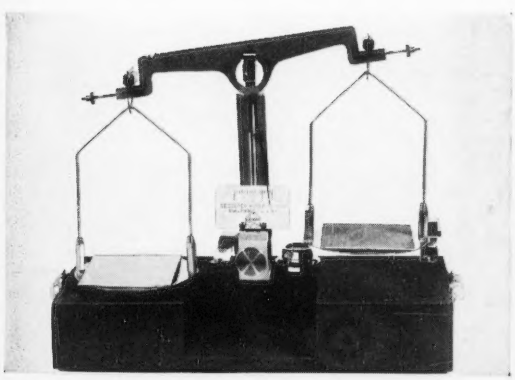
How Rodine Retards Acid's Attack on Metal



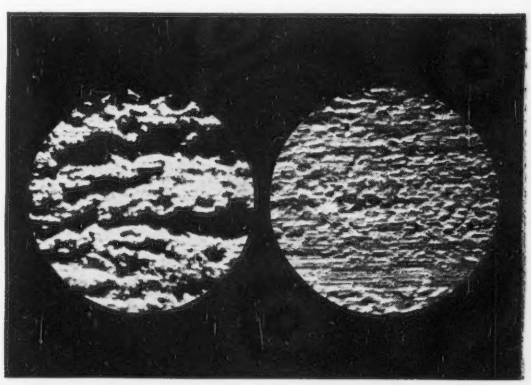
The photographs and microphotographs displayed on this page represent a graphic description of results demonstrating the effectiveness of RODINE in retarding the attack of acid on the metal. NO WEIGHT DIFFERENCE—two identical panels of low-carbon steel are shown being weighed here. They balanced the scale.



RODINE MINIMIZES ACID ATTACK—Each descaled panel was placed in a beaker containing 10% by volume of 66° Bé sulfuric acid of 160° F. The acid in the right-hand beaker was uninhibited. Acid in left-hand beaker was inhibited with RODINE 82, ¼% by volume of the concentrated acid. There was little or no hydrogen evolution in this beaker . . . RODINE retarded the attack of the acid on the base metal.



RODINE SAVES METAL—Both descaled panels were removed from the acid pickle solutions after 5 minutes. The one pickled in the uninhibited acid had lost 1.4% of its original weight. The one pickled in the RODINE-inhibited acid had lost only 0.001% of its original weight. This represents a saving of 26 lb. of steel for each ton pickled; and a simultaneous saving of nearly 50 lbs. of 66° Bé sulfuric acid when RODINE is used to inhibit the acid.



EFFECT OF UNINHIBITED ACID ON THE PANEL — This microphotograph of the low-carbon sheet steel pickled in the uninhibited acid shows deep pits and the crystalline character of the surface after 5 minutes in the solution.

EFFECT OF RODINE-INHIBITED ACID ON THE PANEL — This panel was pickled for 5 minutes in the RODINE-inhibited acid, then microphotographed. Only scale pockets and roll marks are visible; no pitting of the low-carbon sheet steel occurred.

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Schedule Given for Oklahoma Short Course

Sept. 28-30 Sessions To Include Basic and Advanced Subjects

Complete program is given below for the 7th Annual Corrosion Control Short Course sponsored by the University of Oklahoma and the NACE Central Oklahoma Section. The short course will be held September 28-30 at the Extension Study Center on the North Campus of the University of Oklahoma at Norman.

Registrations should be forwarded to M. L. Powers, Director, Business and Industrial Services, Extension Division, University of Oklahoma, Norman, Okla.

Director of the course is Raymond D. Daniels, assistant professor of metallurgical engineering at the University.

Wednesday, Sept. 28

Fundamentals

Chairman John Knox, Halliburton Oil Well Cementing Company.

8-9 am Registration

9:00 Welcome Address by W. H. Carson, dean of College of Engineering, University of Oklahoma, and Response for NACE by Dan Carpenter, Atlas Powder Company.

9:15 Economics of Corrosion Control, by J. D. Sudbury, Continental Oil Company.

10:20 Corrosion in Action, film produced by International Nickel Co., Inc.

Techniques of Corrosion Control

Chairman Frank B. Burns, General Asphalts, Inc.

1:15 pm Physical and Chemical Aspects of Corrosion Inhibition, by Ben F. Davis, Jr., Atlas Powder Company.

2:00 Fundamentals of Protective Coatings, by Glen R. Roberson, Standard Oil Company of Texas.

3:05 Steels in High Temperature Service, by T. M. Krebs, Babcock and Wilcox Company.

3:50 Corrosion Resistant Materials Selector—Non-Metallic, by E. D. Edmisten, Fibercast Corporation.

Thursday, Sept. 29

Techniques of Corrosion Control (cont'd)

Chairman George W. Evans, Southwestern Bell Telephone Company.

8:30 Fundamentals of Cathodic Protection, by Y. W. Titterington, Corrosion Services, Inc.

9:15 Instrumentation for Field Surveys and Cathodic Protection, by J. R. Cowles, Agra Engineering Company.

Cathodic Protections: Pipelines and Distribution Systems

Chairman M. L. Steffens, Oklahoma Natural Gas Company.

10:20 Cathodic Protection With Impressed Current Anodes, by O. W. Everett and R. D. McDonald, Oklahoma Natural Gas Company.

11:05 Cathodic Protection With Sacrificial Anodes, by David H. Burton, Standard Magnesium Corporation.

Cathodic Protection: Oil Production

Chairman George W. Evans, Southwestern Bell Telephone Company.

10:20 Oil Field Casing Cathodic Protection, by J. R. James, Cathodic Protection Service.

11:05 Cathodic Protection of Oil Field Vessels, by C. O. Smith, Humble Oil & Refining Company.

Field Instrumentation and Demonstrations

Chairman Truel E. Adams, Consolidated Gas Utilities Corporation.

1:15-4:45 pm

1. Introduction by Truel E. Adams
2. Soil Resistivity Survey, by Elmer L. Curry, Cities Service Gas Company.
3. Pipe to Soil Potentials Survey, by O. W. Everett, Oklahoma Natural Gas Company.
4. Surface Potentials Survey, by J. R. James, Cathodic Protection Service.
5. Line Current Measurements, by Melvin Barb, Kerr-McGee Oil Company.

For information on four other corrosion control short courses, see Page 47 of the August issue of CORROSION Magazine.

6. Cathodic Protection With Sacrificial Anodes, by D. H. Burton, Standard Magnesium Corporation.
7. Cathodic Protection With Rectifiers, by H. R. Aschan, Good-All Electric Manufacturing Company.
8. Galvanic Relationships of Dissimilar Metals, by C. L. Mercer, Southwestern Bell Telephone Company.

6:30 Banquet with guest speaker

Friday, Sept. 30

Refinery and Pipeline

Chairman Elmer L. Curry, Cities Service Gas Company.

8:30 am *Rectifier* Trouble Shooting, by Harry R. Aschan.

9:15 A Practical Look at Pipeline Coatings, by James C. Bell, Service Pipeline Company.

10:20 Corrosion Control in Recirculating Cooling Water Systems, by P. G. Bird, Wright Chemical Company.

11:05 Paints for Corrosion Protection, by Russ Gillogly, Continental Oil Company.

Oil Production

Chairman John Daly, DX Sunray Mid-Continent Oil Company.

8:30 am Corrosion From Reservoir to Pipeline, by Harry G. Byars, Atlantic Refining Company.

10:05 Application of Down-Hole Corrosion Inhibitors, by Rupert H. Poetker, Sunray Mid-Continent Oil Company.

11:00 Protective Coatings in Water Flood, by Jack Barrett, Pan American Petroleum Company.

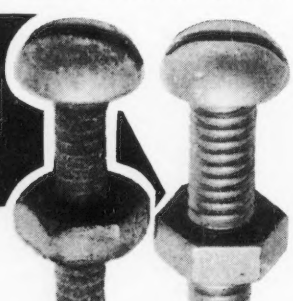
Corrosion Round Table

Chairman D. H. Carpenter, Atlas Powder Company.

1:15 pm *Corrosion* Coordinating Committees, by Charles L. Mercer.

2:00 Round Table Discussion of Specific Corrosion Problems, all speakers participating.

MCC the acid tamer NEW



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NOW ALUMINUM or galvanized can be cleaned by the hydrochloric solution method, without any harmful corrosive effect.

MCC acid corrosion inhibitor, a NEW universal additive for all acids, except nitric, improves acid cleaning solutions for all metals, except magnesium, by inhibiting the surface destroying corrosive effect of the acid without imparing the cleaning qualities. MCC the universal additive is a giant stride forward in acid cleaning techniques.

ALUMINUM BOLTS immersed in identical acid strength for 24 hours. Solution using MCC inhibitor showed no visible effects.

WRITE FOR BULLETIN No. 105

devlimco

DEVELOPMENTS UNLIMITED INCORPORATED
328 BROADWAY PASSAIC, NEW JERSEY

Letters to the Editor

American Zinc Institute
New York 17, N. Y.
July 22, 1960

The Editor, CORROSION.

We have read with interest the case history, "One Corroded, One Did Not —But Both Water Pumps Failed" on page 46 of your July 1960 issue.

We suspect immediately that the original equipment pump with zinc die cast impeller and casing operated in an area where water was significantly corrosive, probably having a low pH and low resistance. Presumably, the manufacturer has used the construction described with success in many operations —otherwise, he would not be using zinc die castings.

The combination of corrosive water in a zinc pump with steel spindle, brass fitting and copper tubing certainly aggravated any normal slow action on the part of the water through the sacrificial attempt of the zinc to protect its metallic neighbors. Though die cast alloys are not the best for cathodic protection, the velocity of the water would inevitably maintain fresh metal surfaces. Presumably, the use of steel for the motor spindle is inescapable. With best construction, it would be galvanized zinc-plated, or cadmium-plated. If brass fittings and copper tubing must be used, they should be suitably insulated from the main body.

This is another example of design without suitable precaution against the creation of galvanic cells and the rapid deterioration of the least noble metal. Zinc pumps, properly used, serve well in millions of appliances—example, washing machines.

Very truly yours,
(Signed): J. L. KIMBERLEY
Executive Vice President

SECTION CALENDAR

September
7 Teche Section. Petroleum Club.
9 Birmingham Section.
12 Greater St. Louis Section. Non-Destructive Test Methods, by John Bobbin, Branson Instruments.
12 Kansas City Section.
12 Central Oklahoma Section.
12 North Texas Section. Torch Restaurant, Dallas, 6:30 pm.
13 San Francisco Bay Area Section.
13 Houston Section. Houston Engineers Club.
13 Permian Basin Section.
15 Detroit Section.
15 Vancouver Section.
20 Cleveland Section.
20 Alamo Section.
26 Tulsa Section.
27 Panhandle Section.
27 Southwestern Ohio Section.

October
3 Teche Section. Petroleum Club.
10 Greater St. Louis Section. Alloys in Process Industries, by John Schley.
10 Kansas City Section.
10 Central Oklahoma Section.
10 North Texas Section. Cathodic Protection Studies, by A. R. Erben. Torch Restaurant, Dallas, 6:30 p.m.
11 San Francisco Bay Area Section.
11 Houston Section. Houston Engineers' Club.
11 Permian Basin Section.
18 Cleveland Section.
18 Alamo Section.
20 Vancouver Section.
24 Tulsa Section.
25 Panhandle Section.
25 San Joaquin Valley Section. Maison Jaussard's Restaurant, Bakersfield, Cal.
25 Southwestern Ohio Section.
25 Genesee Valley Section. Discussion on Penton, by G. M. Taylor, Hercules Powder Co.

•

Western Region's 1960 Conference will be Oct. 6-7 at the Sheraton Palace Hotel in San Francisco, Cal.

Corrosion Control Group Formed in New Zealand

A "Corrosion Prevention Association" has been formed in New Zealand with an initial membership of about 60. A. L. Titchener, Senior Lecturer in Mechanical Engineering at the University of Auckland reports that steps are under way to adopt a set of regulations and establish aims and methods of accomplishing those aims.

A series of monthly meetings of interested people from all walks of engineering and industry have been scheduled for the remainder of the year. Meetings have been held on cost and consequences of corrosion and on the mechanisms of galvanic action.

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Cleveland 5, Ohio • Long Beach 10, California

Canadian Region

Eastern Division Conference to Have Sixteen Papers on Technical Program

Sixteen technical papers are included in the tentative schedule of the November 14-15 conference of the Canadian Region's Eastern Division to be held at the Hotel Royal in Montreal, Quebec.

A schedule of the papers is given below:

Monday, November 14

am

Structure and Composition of Passive Films on Iron, by M. Cohen, National Research Council, Ottawa.

Generalized Description of Metallic Passivity, by N. D. Greene, Rensselaer Polytechnic Institute.

Theory of Alloy Passivity Applied to Stainless Steels, by W. A. Mueller, Pulp and Paper Research Institute of Canada.

pm

Corrosion Resistance of Stainless Steels in Various Applications by G. E. Rowan, Atlas Steels Ltd.

Corrosion Resistant Equipment of Titanium, Zirconium and Tantalum, by C. A. Hampel.

Practical Aspects of and Experience with High Temperature Alloys, by N. J. Zachman, Hayes Alloys Products Co.

Tuesday, November 15

am

Aluminum Corrosion, by H. P. Godard, Aluminium Laboratories Ltd.

Corrosion Experience With Respect to Buildings, P. J. Sereda, National Research Council, Ottawa.

Outdoor Corrosion Tests in Canada, by E. V. Gibbons, National Research Council, Ottawa.

Paint Specifications for Corrosion Prevention, by D. Hargreaves, Sherwin-Williams Company of Canada, Ltd.

pm

New Corrosion Resistant Coating for Mine Hoist Wire Rope, by R. Rogers, Mines and Technical Survey Dept., Ottawa.

Marine Corrosion, by R. D. Taylor, American Smelting and Refining Co.

One paper is to be added to the Tuesday afternoon sessions.

Wednesday, November 16

am

Costs of Corrosion, by C. W. Brickett, Aluminium Company of Canada, Ltd.

Two other papers are to be added to the Wednesday morning sessions.

pm

A round table discussion has been scheduled tentatively to complete the conference.

Canadian Region Officers Elected for 1961 Term

New officers Canadian Region recently elected for 1961 are as follows:

Chairman: H. H. Yates, associate professor of metallurgical engineering at McGill University, Montreal.

Vice Chairman: D. S. McIntosh, chief pipeline engineer with British American Oil Co., Calgary.

Secretary-Treasurer: H. A. Webster, general manager of Corrosion Service Ltd., Toronto.

Membership Chairman W. H. Seager, senior corrosion engineer with Interprovincial Pipe Line Co., Edmonton.

One Set Corrosion Back Issues Is Available

One set of back issue of CORROSION Magazine complete from the first issue in 1945 to January, 1960, bound in 14 volumes is available from an NACE member.

The binding for the 14 volumes is blue buckram with gold lettering on the book spine. Advertising has been deleted from all issues except those for December, which is the index issue for each year.

Persons interested in purchasing this set of back issue should contact Ansel L. Conns, 3159 South Stafford St., Arlington 6, Va.

POSITIONS WANTED AND AVAILABLE

Active and Junior NACE members and companies seeking salaried employees may run without charge two consecutive advertisements annually under this heading, not over 35 words set in 8 point type. Advertisements to other specifications will be charged for at $10 a column inch.

Positions Available

Positions
in
CORROSION RESEARCH

Need experienced men for work on corrosion problems associated with petroleum and chemical industries. Positions require imaginative, aggressive, graduate level physical or electro chemists. Salary dependent on experience and training. Write:

Attn: Mr. E. J. Farrell
STANDARD OIL COMPANY (Ind.)
P. O. Box 431-A Whiting, Indiana

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Challenging position available in research to study stress corrosion characteristics of aluminum alloys. B.S. degree minimum requirement. Metallurgy, corrosion or physical chemistry experience in nonferrous metals desirable. Salary commensurate with academic training and experience. Excellent employee benefit programs, relocation cost paid by company. Direct resume of academic training and experience to:

Dr. T. R. Pritchett
Kaiser Aluminum & Chem. Corp.
Dept. of Metallurgical Research
Spokane 69, Washington

Positions Available

Corrosion Engineer, to be sales consultant on patented corrosion-resistant tubular steel products on part time basis. Chemical or petroleum refinery experience helpful. New York City vicinity. Send resume to CORROSION, Box 60-28.

Positions Wanted

Engineer—Nine years' experience electrochemistry and Diesel, gasoline engines with corrosion emphasis. Other experience research and development, heavy in instrumentation. Want full-time corrosion position. Age 39. BS physics. CORROSION, Box 60-25.

Corrosion Engineer—Seven years' corrosion control and three years' diversified experience with both gas distribution and pipeline companies. BS in Ch.E. Married, will relocate. Resume on request. CORROSION, Box 60-26.

Sales-Promotion, 13 years successful industrial sales engineering experience in chemicals and corrosion resistant materials. Age 37, chemistry graduate, marketing post-graduate. Chicago preferred, Midwest travel. Familiar direct and distributor sales. Resume available. CORROSION Box 60-27

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The 1960 North Central Region Conference will be held Oct. 19-20 at the Schroeder Hotel in Milwaukee, Wis.

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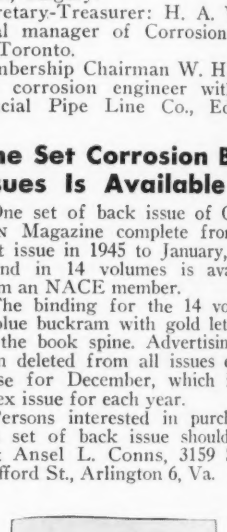
The 1960 South Central Region Conference will be held October 25-28 at the Mayo Hotel, Tulsa, Okla.



Over 1000 Articles In Corrosion 1945-60 Listed

Over 1000 articles published in CORROSION in the last 15 years are listed by subject matter. Each article includes the price for a copy, so you can select those in which you are interested and know exactly how much they will cost without further inquiry. Very valuable for research workers in the corrosion field. Complete through June, 1960.

Write for a FREE COPY, or indicate your field of special interest for a list covering your interest only.

DEATHS

Former NACE President Norton E. Berry Dies

Norton E. Berry, 1951-52 president of NACE died July 8 at his home in Tucson, Arizona, after a long illness. A member of NACE since 1946, he was active in the association in arranging technical programs, as a member of the board of directors representing North Central Region and as vice president and president. He also was vice chairman of the Inter-Society Corrosion Committee in 1954.

At the time he joined NACE, Mr. Berry was director of research for Servel, Inc., at Evansville, Ind. He then had been working on corrosion problems for 15 years, an interest that he pursued to the time of his death. He held a BS and PhD in physical chemistry from the University of California.

BERRY

In 1955, he left Servel to join Mallinckrodt Chemical Works in St. Louis, Mo., where he was occupied with various problems of that company's uranium division. After he became seriously ill in late 1959, he moved to Tucson and continued corrosion consulting work until his death.

He is survived by his wife, a daughter, Mrs. Gerald Wheatley of Vancouver, B. C., and a son, Richard Norton Berry of St. Joseph, Mo.

•

Norman T. Shideler, an NACE member and author of several technical papers on corrosion control, died July 14. He had been working as a corrosion consultant and formerly was affiliated with Pittsburgh Chemical Company.

•

Harry N. Strothman, NACE member who was Chicago regional sales manager for Royston Laboratories, Inc., died July 7 at his home in Park Forrest, Ill.

NACE Member in Israel to Be ISCC Correspondent

NACE member D. Spector. Citrus House, 22 Harakevet St., Tel Aviv, Israel, has agreed to act as the Inter-Society Corrosion Committee correspondent for Israel.

With this appointment, the total number of countries reporting to ISCC is 18, according to Hugh P. Godard, chairman of the ISCC Subcommittee on Foreign Relations.

•

NACE's 17th Annual Conference and 1961 Corrosion Show will be March 13-17, 1961, at the Hotel Statler in Buffalo, N. Y.

•

Northeast Region's 1960 Conference will be October 11-14 at the Prichard Hotel, Huntington, W. Va.

•

The 1960 North Central Region Conference will be held Oct. 19-20 at the Schroeder Hotel in Milwaukee, Wis.

Hawaiians Show Increased Interest in NACE Group

Progress in gaining members in NACE preliminary to organizing a corrosion control group in Hawaii is reported by H. A. Morley, Pearl Harbor Naval Shipyard, Honolulu. Mr. Morley says that he is meeting with success in securing new members and expects to have a sufficient number to petition for recognition as an NACE Section soon.

The question of organizing sections outside of the North American continent is on the agenda of the NACE board for consideration at coming meetings. The present articles of organization restrict the association to the continent.

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TECHNICAL REPORTS

on

REFINING INDUSTRY CORROSION

T-8 High-Temperature Hydrogen Sulfide Corrosion of Stainless Steel—A Contribution to the Work of NACE Tech. Group Committee T-8 on Refinery Industry Corrosion, by E. B. Backensto, R. E. Drew, J. E. Prior and J. W. Sjoberg. Pub. 58-3, Per Copy $1.50.

T-8 Compilation and Correlation of High Temperature Catalytic Reformer Corrosion Data—A Contribution to the Work of NACE Tech. Group Committee T-8, by G. Sorell. Pub. 58-2, Per Copy $3.00.

T-5B-2 Effect of Sulfide Scales on Catalytic Reforming and Cracking Units. Part 1—Metallographic Examination of Samples From a Catalytic Reforming Unit. Part 2—Intergranular Corrosion of 18-8 Cr-Ni Steel as a Result of Hydrolysis of Iron Sulfide Scale. A Contribution to the Work of NACE Task Group T-5B-2 on Sulfide Corrosion at High Pressures and Temperatures in the Petroleum Industry. Per Copy $1.50.

T-5B-2 Collection and Correlation of High Temperature Hydrogen Sulfide Corrosion Data—A Contribution to the Work of NACE Task Group T-5B-2 on Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry: From M. W. Kellogg Co., New York by G. Sorell and W. B. Hoyt. Pub. 56-7. Per Copy $5.50.

T-5B-2 High Temperature Hydrogen Sulfide Corrosion in Thermofor Catalytic Reformers—A Contribution to the Work of NACE Task Group T-5B-2 on Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry: From Socony Mobil Oil Co., Inc., Res. & Dev. Lab., Paulsboro, N. J. by E. B. Backensto, R. D. Drew, R. W. Manuel and J. W. Sjoberg. Pub. 56-8. Per Copy $2.50.

T-5B-2 Effect of Hot Hydrogen Sulfide Environments on Various Metals—A Contribution to the Work of NACE Task Group T-5B-2 on Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry: From Sinclair Res. Lab. Inc. Harvey, Ill. Pub. 57-2. Per Copy $3.00.

T-5B-2 High Temperature Sulfide Corrosion in Catalytic Reforming of Light Naphthas—A Contribution to the Work of NACE Task Group T-5B-2 on Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry: From Humble Oil & Ref. Co., Baytown, Texas. Pub. 57-3. Per Copy $1.50.

T-8 Iso-Corrosion Rate Curves for High Temperature Hydrogen-Hydrogen Sulfide—A Contribution to the Work of NACE Tech. Group Committee T-8, by E. B. Backensto and J. W. Sjoberg. Pub. 59-10. Per Copy $1.50.

T-8 Minimum Corrosion for Butane Isomerization Units. A Contribution to the Work of NACE Group Committee T-8 on Refining Industry Corrosion by J. F. Mason, Jr. and C. M. Schillmoller. Pub. 59-11. Per Copy $1.50.

T-8 Corrosion of Refinery Equipment by Aqueous Hydrogen Sulfide. A Contribution to the Work of Group Committee T-8 on Refining Industry Corrosion by Roy V. Comeaux. Pub. 59-12. Per Copy $1.50.

T-8A Precautionary Procedures in Chemical Cleaning. A Contribution to the Work of NACE Tech. Unit Committee T-8A on Chemical Cleaning, by Robert A. Stander. Pub. 59-1. Per Copy $1.50.

T-8A Chloride Stress Corrosion Cracking of the Austenitic Stainless Steels—A Contribution to the Work of NACE Task Group T-8A on Chemical Cleaning, by J. P. Engle, C. L. Floyd and R. B. Rosene. Pub. 59-5. Per Copy $1.50.

Remittances must accompany all orders for literature the aggregate cost of which is less than $5. Orders of value greater than $5 will be invoiced if requested. Send orders to National Association of Corrosion Engineers, 1061 M & M Bldg., Houston, Texas. Add 65c per package to the prices given above for Book Post Registry to all addresses outside the United States, Canada and Mexico.

NATIONAL ASSOCIATION OF CORROSION ENGINEERS

1061 M & M Bldg. Houston 2, Texas

One-Third Corrosion Show Booth Spaces Already Contracted

About one-third the available space for exhibition booths at the 1961 Corrosion Show has been requested, only 30 days after the information brochures were mailed to prospective exhibitors.

The 1961 Corrosion Show will be held in conjunction with the 17th Annual NACE Conference at Buffalo, N. Y., March 13-17. The Corrosion Show and the majority of activities of the conference will be held on the same floor of the Hotel Statler-Hilton, according to R. W. Huff, Jr., NACE Exhibits Manager, thus giving conference registrants convenient access to the Corrosion Show exhibits.

No technical symposia meetings have been scheduled for the afternoon of March 14, the Corrosion Show's opening day so that all registrants can attend the show.

Names of companies which have contracted for exhibition space at the Corrosion Show to date are as follows:

Aluminum Company of America
Amercoat Corporation
Carboline Company
Clementina Limited
Crucible Steel Company
Delaware Barrel & Drum
Dow Chemical Company
Fibercast Company
Garlock, Inc.
Glidden Company
Gray Company
Harco Corporation
Heil Process Equipment Corporation
International Nickel Co., Inc.
Knapp Mills, Inc.
Minnesota Mining & Mfg. Company
National Carbon Company
Pittsburgh Corning Corporation
Reilly Tar & Chemical Company
Royston Laboratories, Inc.
Standard Magnesium Corporation
U. S. Stoneware
T. D. Williamson, Inc.

Corrosion Division Program to Include 19 NACE Members

Nineteen NACE members will participate in the October 10-13 program of the Corrosion Division of the Electrochemical Society at the Shamrock-Hilton Hotel, Houston, Texas. They will be chairmen of the Corrosion Division's various symposia and authors of technical papers to be presented.

An alphabetical listing of these NACE members is given below with their company affiliations.

F. M. Beck of Ohio State University, Columbus, Walter Roger Buck, III, of Virginia Institute for Scientific Research, Richmond, Andrew Dravnieks of Standard Oil of Indiana, Whiting, Ind., Samuel A. Evans of J. M. Huber Corp., Borger, Texas.

Robert T. Foley of General Electric Co., Schenectady, N. Y., M. G. Fontana of Ohio State University, Columbus, Ohio, N. D. Greene of Rensselair Polytechnic Institute, Troy, N. Y., Norman Hackerman of the University of Texas, Austin, Texas, Ray M. Hurd, Texas Research Associates, Austin, Texas.

C. V. King of New York University, New York, N. Y., Ernest L. Koehler of Continental Can Co., Inc., Chicago, Ill., A. C. Makrides of Union Carbide Metals Co., Niagara Falls, N. Y., Glenn A. Marsh of Pure Oil Co., Crystal Lake, Ill., Robert A. Powers of Union Carbide Consumers Products Co., Cleveland, Ohio.

Olen L. Riggs, Jr., of Continental Oil Co., Ponca City, Okla., Edward Schaschl of Pure Oil Research & Development Laboratories, Crystal Lake, Ill., D. A. Shock of Continental Oil Co., Ponca City, Okla., John D. Sudbury of Continental Oil Co., Ponca City, Okla., and H. H. Uhlig of Massachusetts Institute of Technology, Cambridge, Mass.

Color Slide-Talk on 1960 Corrosion Show

A 35-mm color slide show of about 100 slides of exhibits at the 1960 Corrosion Show at Dallas has been prepared and is available for showing at NACE Section meetings. The show, which has a commentary on specific items exhibited, is available on a first-come, first-served basis on application to G. A. Rolak, NACE Central Office.

The show provides an opportunity for NACE members who were unable to visit the Corrosion Show personally to see some of the equipment on display. While the presentation does not include all the exhibits, it will give a good idea of the show. Presentation time should vary between an hour and an hour and a half.

how CORROSION is indexed

- **By Volumes Annually in December Issue**
- **In NACE Bibliographic Surveys of Corrosion**
- **In NACE Abstract Punch Card Service**
- **In 10-Year Index to CORROSION**
- **In Engineering Index**
- **In Applied Science and Technology Index**

NATIONAL and REGIONAL MEETINGS and SHORT COURSES

1960

Oct. 6-7—10th Annual Western Region Conference, Sheraton-Palace Hotel, San Francisco, Cal.

Oct. 6-8—Southeast Region Conference, Dinkler-Plaza Hotel, Atlanta, Ga.

Oct. 11-14—Northeast Region Conference. Prichard Hotel, Huntington, W. Va.

Oct. 19-20—North Central Region Conference. Pfister Hotel, Milwaukee.

Oct. 25-27—South Central Region Conference. Mayo Hotel, Tulsa.

November 14-16—Eastern Division, Canadian Region Conference, Hotel Royal, Montreal.

November 17-18—NACE Board of Directors Meeting, Sherman Hotel, Chicago, Ill.

1961

March 12—NACE Board of Director's Meeting, Hotel Statler, Buffalo, N. Y.

March 13-17—17th Annual Conference and 1961 Corrosion Show, Buffalo, N. Y., Hotel Statler.

March 17—NACE Board of Director's Meeting, Hotel Statler, Buffalo, N. Y.

Oct. 4-6—Western Region Conference, Hotel Multnomah, Portland, Oregon.

Oct. 9-11—North Central Region Conference, St. Louis, Chase Park Plaza Hotel.

Oct. 24-27—South Central Region Conference and Exhibition, Shamrock-Hilton Hotel, Houston.

Oct. 30-Nov. 2—Northeast Region Conference, New York City, Hotel Statler.

Southeast Region Conference, Miami, Fla., in conjunction with Miami Section's short course.

1962

March 19-23—18th Annual Conference and 1962 Corrosion Show. Kansas City, Municipal Auditorium.

October 1-4—Northeast Region Conference, Hotel Sheraton Ten Eyck, Albany, N. Y.

October 9-11—North Central Region Conference.

October 16-19—South Central Region Conference and Exhibition, Granada Hotel, San Antonio.

SHORT COURSES

1960

September 12-16—Short Course on Process Industry Corrosion, sponsored by NACE Technical Committee T-5 and Ohio State University, to be held at Ohio State University, Columbus.

September 28-30—Central Oklahoma Section 1960 Corrosion Control Short Course, at University of Oklahoma, Norman.

October 3-5—Corrosion Control Short Course, sponsored by Western Region and University of California, San Francisco.

October 12-13—San Joaquin Valley Section Biannual Corrosion Tour Registration at Bakersfield Inn, Bakersfield, Calif.

November 7-11—Annual Florida General Conference Corrosion Short Course, Key Biscayne Hotel, Miami. Sponsored by Miami and Jacksonville Sections.

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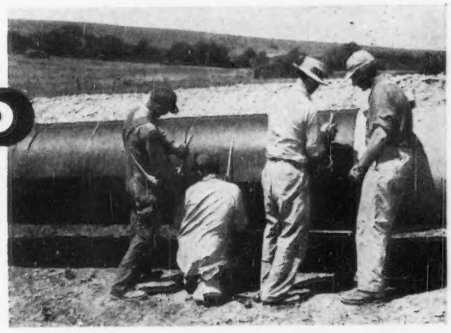

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Foreign Corrosion Reports

New Zealand Corrosion Activity

A report on corrosion activity for 1959 from New Zealand printed below has been received by the Inter-Society Corrosion Committee's Subcommittee on Relations with Foreign Organizations.

Activities in Department of Scientific and Industrial Research

1. Corrosion investigations related to use of geothermal steam are continuing with emphasis on investigations of sulfide stress cracking, a quantitative study of the diffusion of hydrogen in steels exposed to H_2S solutions at temperatures to 240 C, types of corrosion product (*NZJ Sci*, **2**, 422-430, 1959) and stress rupture properties of steels.

2. Studies of corrosion behavior of copper and copper brazing alloys in the reticulation of hot and cold New Zealand waters are continuing. Consideration is being given to causes of localized corrosion. (*J Electrochem Soc*, **106**, 468, 1959).

3. Corrosion tests in a volcano crater lake and in the river seasonally fed by the lake have been completed. (*NZJ Sci*, **3**, 93-99, 1960).

4. Long term investigations in underground corrosion are continuing.

5. Investigations of the intergranular corrosion of duralumins have been concluded (*J Appl Chem*, **9**, 28, 1959; *J Appl Chem*, **10**, 138, 1960).

Activities in Other Government Departments

The corrosive effects of preservative chemicals in treated timbers are being investigated by the New Zealand Forest Service.

Activities by University of Canterbury

Some work has been done on the corrosion of iron (*Chem. and Ind.* 727, 1959).

Investigations are continuing in the behavior of aluminum. The mechanism of pitting (*J Appl Chem*, **9**, 323-330, 1959) and the electrode behavior (being prepared for publication) are chief subjects of interest.

Commercial Activities

Investigations of corrosion by geothermal steam are being conducted by Tasman Pulp and Paper Company, Kawerau. No other systematic private studies are known to have been conducted in 1959.

Ian K. Walker, Director
Dept. of Scientific and Industrial Research Dominion Laboratory
P. O. Box 8023
Wellington, New Zealand

•

About $15 million worth of Christmas tree light bulbs were purchased in the United States for the 1959 Yuletide season.

•

CORROSION's index appears in December.

•

NACE's Bibliographic Surveys of Corrosion extend from 1945 to 1955. Prices available upon request.

Focus on Plastics for Process Equipment

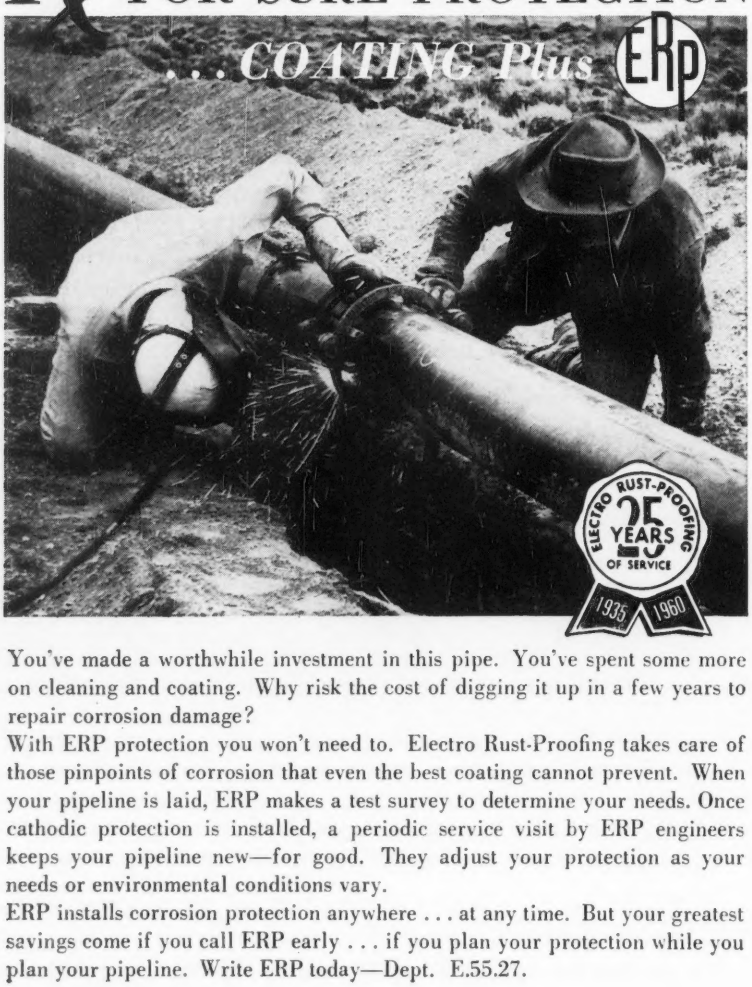
The November issue's Technical Topics Section will be devoted to discussing the use of plastics for process equipment. Other interesting articles on plastics will be featured in that issue also.

Technical Topics Included in Index

Technical Topics will be included in CORROSION's annual index published in the December issue. The Topics will be cross-referenced in the alphabetical subject and author index.

Persons who customarily extract Technical Section pages from each issue for binding are reminded that the Technical Topics pages should be extracted also for a more complete reference to technical information published in CORROSION.

Rx FOR SURE PROTECTION



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With ERP protection you won't need to. Electro Rust-Proofing takes care of those pinpoints of corrosion that even the best coating cannot prevent. When your pipeline is laid, ERP makes a test survey to determine your needs. Once cathodic protection is installed, a periodic service visit by ERP engineers keeps your pipeline new—for good. They adjust your protection as your needs or environmental conditions vary.

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CORROSION ABSTRACTS

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1. GENERAL

1.2 Importance

1.2.5, 6.4.4, 3.8.4, 4.3.2, 8.8.5

Pyrophoricism in Metals. Henry Allen. Metal Treatment and Drop Forging, **26**, No. 160, 31-32 (1959) January.

It has been observed that if magnesium die-castings are immersed for a prolonged period in chromic acid solution, an ignition risk arises. It is recommended that magnesium die-castings be washed immediately on removal from the solution in cold water, afterwards being coated with mineral oil. The theory is that the prolonged immersion in the chrome creates a finely divided condition and that with magnesium die-castings, for instance, a precipitate is formed, such as a magnesium-aluminum compound in a fine particle form. When dried in air, the large surface of the powdery film exposed to oxidation with consequent evolution of heat, may touch off spontaneous ignition. There are some hazardous chemical combinations also, to take an illustrative case, methyl chloride in contact with aluminum can form spontaneously combustible aluminum methyl. Boron trifluoride is said to be highly effective for the control of fire risk in heat-treatment furnaces using magnesium. In machine shops where pyrophoric metals are worked the meticulous removal of dust and sludge is the most effective safety measure.—ALL. 18235

1.2.2, 8.9.3, 5.2.1

Costs of Cathodic Protection on Underground Pipelines. (In German.) G. Reuter. Gas-u. Wasserfach., **100**, No. 33, 857-860 (1959) August 14.

That the cost of cathodic protection is cheaper the earlier it is applied is indicated by calculated cost data for German gas and water pipelines, of total length 224 km., protected by magnesium anodes and for pipelines of total length 217 km., protected by impressed current installations. 18525

1.2.2, 2.1.1, 5.2.1

Cathodic Protection of (Buried) Piping by Means of Impressed Currents: Economic Study. (In French.) H. M. Powell and J. H. Morgan. Corrosion et Anticorrosion, **7**, No. 1, 20-26; disc., 26 (1959).

A method of calculating costs of cathodic-protection installations with a view to economic operation is described. Mathematical bases for the calculations are presented. French legal statutes concerning cathodic protection are mentioned in the discussion.—MA. 18504

1.2.5, 6.3.15, 6.3.20, 3.4.6, 4.6.2

Reactions of Metals with Oxygen and Steam. Final Report for June 15, 1958 to February 15, 1959. Fred E. Littman and Frank M. Church. Stanford Res. Inst. for Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., AECU-4092, Feb. 15, 1959, 25 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

Titanium, zirconium and Zircaloy can spontaneously ignite under relatively

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BTR—Battellee Technical Review, Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio.

CO—Centre d'Information du Cobalt, 35 Rue des Colonies, Brussels 1, Belgium.

EL—Electroplating and Metal Finishing, 85 Udney Park Road, Teddington, Middlesex, England.

GRR—U. S. Government Research Reports, Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

HB—Translations, Henry Brutcher, P. O. Box 157, Altadena, California.

IIM—Transactions of The Indian Institute of Metals, 31 Chowringhee Rd., Calcutta 16, India.

INCO—The International Nickel Co., Inc., 67 Wall Street, New York 5, New York.

JSPS—Japan Society for the Promotion of Science, Mr. Hayata Shigeno, Secretary, Committee of Preventing Corrosion, c/o Government Chemical Industrial Research Institute, 1 Chome Nakameguro, Meguro-Ku, Tokyo, Japan.

MA—Metallurgical Abstracts, Institute of Metals, 17 Belgrave Square, London SW 1, England.

NALCO—National Aluminate Corp., 6216 West 66th Place, Chicago 38, Illinois.

NSA—Nuclear Science Abstracts, United States Atomic Energy Commission, Technical Information Division, Oak Ridge, Tennessee.

OTS—Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

PDA—Prevention of Deterioration Abstracts, National Research Council, 2101 Constitution Ave., Washington 25, D. C.

PI—Pergamon Institute, 1404 New York Ave., N. W., Washington 5, D. C.; Oxford and London, England.

PMR—Platinum Metals Review, Johnson, Matthey and Co., Ltd., 73-83 Hatton Garden, London, E.C. 1, England.

RIM—International Union of Testing and Research Laboratories for Materials and Structures, RILEM Bulletin, 12, Rue Brancion, Paris XV, France.

RML—Review of Metal Literature, American Society for Metals, 7301 Euclid Ave., Cleveland 3, Ohio.

RPI—Review of Current Literature Relating to the Paint, Colour, Varnish and Allied Industries, Research Assoc. of British Paint, Colour and Varnish Manufacturers, Paint Research Station, Waldegrave Rd., Teddington, Middlesex, England.

SE—Stahl und Eisen, Verlag Stahleisen, m.b.H., Breite Strasse 27 (Schliessfach 2590), Dusseldorf, Germany.

TIME—Transactions of The Institute of Marine Engineers, The Memorial Bldg., 76 Mark Lane, London EC 3, England.

TT—Technical Translations, Office of Technical Services, U. S. Department of Commerce, Washington 25, D.C.

ZDA—ZDA Abstracts, Zinc Development Association, 34 Berkeley Square, London W 1, England.

mild conditions. The effect of temperature, oxygen concentration and pressure and the nature of the daluent on the spontaneous ignition of titanium, zirconium and Zircaloy were investigated. —NSA. 18391

1.3 Reviews

1.3, 6.3.15, 5.3.2, 5.4.2

Titanium Coating Program. Phase I: Literature Survey. Interim Report I. W. H. Schaefer, Jr. and H. B. Bombarger. Crucible Steel Co. of America Research Division, Pittsburgh, October 15, 1958, 33 pp. Contract AF33 (600)-37425.

A survey was made of coating literature and organizations were contacted who may have an interest in the high-temperature protection of titanium during fabrication. High-temperature protection is the most important quality sought, but characteristics such as ease of application, green or unfired adhesion, and high-temperature bonding must also be considered. Protective coatings include ceramic, metallic, inorganic and organic materials alone or in combination. Methods of application include spraying, dipping, brushing, electroplating, vapor deposition and flame spraying. Possible ceramic coating compositions are numerous with the effective temperature range being determined by the refractory-flux ratio. For this application, some of the fluxes are refractory enough to be used alone. Hot-dipped aluminum coatings are the most widely studied metallic coatings for titanium. A nickel-plated coating is said to increase hydrogen pickup rather than reduce it. It appears that a coating will have to be developed if it is to meet all of the important qualities. (auth)—NSA. 18931

1.3, 6.4.2, 4.6.1

Aqueous Corrosion of Aluminum at Elevated Temperatures. A Preliminary Literature Survey. Joseph Yahalom. Atomic Energy Commission, Tel-Aviv, Israël, December, 1958, 25 pp. (LS-41).

TECHNICAL REPORTS on MARINE COATINGS

T-1M Suggested Coating Specifications for Hot Application of Coal Tar Enamel for Marine Environment. A Report of NACE Technical Unit Committee T-1M on Corrosion of Oil & Gas Well Producing Equipment in Offshore Installations. Publication No. 57-8. Per Copy $1.50

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A literature survey is presented which is intended to give a general idea of the aluminum corrosion problems discussed in the literature and present the suggestions offered by some authors. The sources are listed in the bibliography. The papers were selected, and only those dealing closely with the subject are given.—NSA. 19000

1.4 Bibliographies and Indexes

1.4, 3.2.2, 6.2.3, 6.3.15

Bibliography on the Effects of Hydrogen Embrittlement of Metals: 1952 to Present. Patricia E. Bell, Compiler. Los Alamos Scientific Lab. U. S. Atomic Energy Commission Pubn., LAMS-2283, December 10, 1958, 19 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

A bibliography concerned chiefly with the effects of hydrogen on steel and titanium is presented. Literature searched included ASM Review of Literature, Volumes 9 through 14, Battelle Technical Review, Volumes 4 and 5, Chemical Abstracts, Volumes 47 through 50, Nuclear Science Abstracts, Volumes 8 through 11 and part of Volume 12, and LASL card catalogs. 108 references.—NSA. 18075

1.4

New Corrosion Index Shows Nation's Rust Pattern. Iron Age, **182,** No. 9, 54-56 (1958) August 28.

An accurate picture of relative rusting rates in every major U. S. city.—BTR. 16760

1.4

Bibliography on Filing, Classification and Indexing Systems for Engineering Offices and Libraries. ESL Bibliography No. 14, 33 pp., 1960. Compiled by Engineering Societies Library, 29 West 39th St., New York 16, N. Y.

One hundred and fifty-five abstracts of articles dealing with systems for the filing and classification of technical information. Two of the three systems organized for corrosion pertain to the NACE Abstract Filing System. A wide variety of generalized and specialized systems are considered, most of them prepared by working engineers. 19106

1.4, 4.4.7, 4.2.3

Bibliography of a Decade of Research on Oil-Ash Corrosion by Heavy Fuels (1948-1958). H. W. Schwab. U. S. Naval Eng. Exper. Station. J. Am. Soc. Naval Engrs., **70,** No. 4, 761-771 (1958) Nov.

Lists over 150 technical papers, articles, etc. on oil-ash corrosion problems, with designations indicating that material in respective article is chiefly concerned with oil-ash problem from: gas turbine application, steam power application, or experimental approach to problem. In brief survey of the topic, parameters which influence the corrosion phenomena are listed.—INCO. 18957

1.6 Books

1.6, 8.1.1, 8.1.3

Corrosion and Its Prevention. Pamphlet, 1958 Edition. 25 pp. Available from Air Conditioning and Refrigeration Inst., 1346 Connecticut Ave., N. W., Washington 6, D. C.

Corrosion as it affects air conditioning and refrigeration industry. Atmospheric, water circuit corrosion, refrigerant circuit corrosion and industry practice and recommendations for combating corrosion. 8 references.—MR. 16738

1.6, 3.8.4

Surface Chemistry, Theory and Applications. J. J. Bikerman. Book, 2nd Edition, 1958, 501 pp. Published by Academic Press Inc., New York; Academic Books Ltd., London.

The second edition of this standard work on surface chemistry, which was first published in 1948, has been brought up to date by thorough revision and the addition of some new material, particularly on electric double layers. The book is divided into six sections, dealing with liquid-gas, liquid-liquid, solid-gas, solid-liquid, three phase systems and electric surface phenomena. In particular, the discussion of solid-liquid systems will be of importance to the electrochemist engaged in metal finishing research. 16536

1.6, 8.4.5, 3.5.4

Materials for Nuclear Reactors. Bernard Kopelman, Editor. Book, 1959, 416 pp. Available from McGraw-Hill Book Co., Inc., 327 West 41st St., New York 36, New York.

Fuel element material is considered from ore through chemical reprocessing of irradiated, spent fuel elements. The properties, chemical, physical and mechanical, of the many other materials that are found within a nuclear reactor are examined, including irradiation behavior. The broad categories of materials studied include fluids, moderators, shielding and control rod materials. —NSA. 18397

1.6, 3.5.8

Metal Fatigue. J. A. Pope, Editor. Lectures Read at a Week's Residential Course at Nottingham University in September 1955. Book, 1959, 381 pp. Available from Chapman and Hall Ltd., London.

Contents: J. A. Pope, "Theory of Fatigue Failure"; "Criteria of Failure under Complex Stresses"; "Stress-Concentration Factors"; "Residual Stresses and Their Effect on Fatigue"; "Cumulative Damage in Fatigue"; J. A. Pope and N. T. Bloomer, "Statistics as Applied to Fatigue Testing"; R. B. Waterhouse, "Corrosion Fatigue and Fretting Corrosion"; A. J. Fenner, "Crack Propagation in Steel Specimens"; P. G. Forrest, "The Effect of Temperature Upon the Fatigue Properties of Steel"; P. H. Frith, "The Fatigue Properties of High-Temperature Alloys"; G. Forrest, "The Fatigue Properties of Aluminium Alloys"; H. Morrogh, "The Fatigue Properties of Cast Iron"; J. W. Cuthbertson, "The Fatigue Properties of Brasses, Bronzes and Bearing Metals" (see Metallurgical Abstracts, **25,** 503); P. L. Teed, "The Fatigue of Aircraft"; B. E. Stephenson, "Fatigue Properties of Joints"; J. G. Whitman, "Fatigue Properties of Welds"; J. Taylor, "Fatigue Loads and Their Effects on Aircraft Structures"; H. L. Cox, "Reproducibility of Results in Fatigue Testing"; J. W. Cuthbertson, "The Fatigue Testing of Bearings"; A. P. Newman, "The Fatigue Testing of Welded Structures"; R. J. Atkinson, "The Fatigue Testing of Aircraft Structures."—MA. 18511

1.6, 6.3.9

Fabrication of Molybdenum. American Society for Metals. Book, 1959, 221 pp. Available from the Society, 7301 Euclid Ave., Cleveland 3, Ohio.

Contents: J. J. Harwood, "Molybdenum as a Structural Material"; G. A.

Timmons, "Development of Molybdenum-Base Alloys"; W. L. Bruckart, "The Production and Quality of Molybdenum Mill Products"; D. C. Martin, "Welding of Molybdenum"; G. S. Hoppin III, "Brazing of Molybdenum"; J. B. Jones, "Ultrasonic Welding"; J. S. Sohn, "Fusion Welding of Molybdenum Power-Plant Components"; R. I. Jaffee, "Protective-Coating Systems for Molybdenum"; W. A. Taebel and J. Gelok, "Machining of Molybdenum and Its Alloys"; R. A. Quadt, "Press Extrusion of Molybdenum Tubing"; D. C. Goldberg, "Forming of Clad Molybdenum"; J. J. Russ, "Forging of Molybdenum and Its Alloys"; R. C. Downey, "Testing in the Hot-Rod Engine"; M. A. Levinstein, "Coating Development and Evaluation"; R. W. Yancey, "Fabrication of Electronic-Tube Components"; J. M. Siergeij, "Missile Structures and Power Plants"; E. H. Edwards, "Molybdenum Requirements in the Petrochemical Industry"; C. C. Woolsey, "Molybdenum Requirements in the Nuclear-Energy Field."—MA. 18303

1.6, 8.9.1, 5.3.4, 5.9.1, 5.4.5

Causes and Prevention of Corrosion in Aircraft. T. C. E. Tringham. Book, 1958, 129 pp. Sir Isaac Pitman & Sons, Ltd., London.

Sources of corrosion in the manufacturing processes of aircraft are described. Storage procedures for raw materials and finished parts are presented. Causes of corrosion in aircraft in service are reviewed. The causes and prevention of corrosion in engines and their associated components are described. Corrosion in aircraft electrical equipment is described. Methods of cleaning metals prior to electroplating are reviewed. Electroplating processes for various metals are discussed. The anodic oxidation of aluminum and chromating of magnesium is discussed. The principal uses of the metallizing processes in the aircraft industry is to provide a protection against heat and corrosion on engine exhaust system components and such items. The pretreatments of various metals prior to painting are presented. The application of paints, enamels, varnishes and resins for protecting aircraft components is discussed. The examination of aircraft parts and structures for defects by one or more of the non-destructive processes is discussed. The salvage of aircraft components from water is discussed.—NSA. 18033

1.6, 2.4.3, 2.3.9

Progress in Non-Destructive Testing: Volume 1. E. G. Stanford and J. H. Fearon, Editors. Book, 1958, 268 pp. Available from Heywood & Co., Ltd., London.

This is the first of an annual series of international volumes containing critical reviews of special aspects of the general subject. In this series it is intended to publish reports on the progress made in relating the properties of materials to each other and to the structural factors which produce them, as well as to survey the six principal methods of flaw detection—visual examination, penetrant testing, magnetic testing, radiography, eddy-current testing and ultrasonic testing. Subjects dealt with in this volume include: recent developments in industrial radiography; stress wave propagation as applied to the detection of flaws by ultrasonic inspection; electromagnetic methods of testing metals; neutron radiography; and the thermal conductivity as a non-destructive testing technique.—ZDA. 18955

1.6, 3.2.2, 8.7.2

Corrosion of Chemical Apparatuses. Corrosive Cracking and Method of Prevention. (In Russian.) G. L. Shvarts and M. M. Kristal. Book, 1958, 204 pp. Available from: State Scientific Technical Publishing House of Machine Building Literature, Moscow, USSR.

The problems of intercrystalline corrosion taking place under static tension in various materials and alloys used in machines and apparatuses for chemical uses are discussed. The principal causes of such corrosion are discussed. Practical examples of deterioration of machinery in industry and methods for preventing corrosive deterioration of metals are described. The book was designed for technicians and technologists working in chemical machine building plants and in the chemical industry.—NSA. 18943

1.6, 6.5, 3.5.9

Sheet Materials for High-Temperature Service. American Society for Metals. Papers presented at the First Southwestern Metal Congress, held at Dallas, Texas, May 12-16, 1958. Book, 1959, 74 pp. Available from the Society, 7301 Euclid Avenue, Cleveland, Ohio.

Contents include: H. R. Ogden, "High Alloys of Chromium, Cobalt, Niobium, Molybdenum and Vanadium"; N. Cannistraro, "Ceramic Coatings for Protection of High-Temperature Materials"; J. E. Starr, "Electrical Strain Measurements at High Temperature"; J. C. Herr, "Joining and Inspection of Joints."—MA. 19010

3. CHARACTERISTIC CORROSION PHENOMENA

3.8 Miscellaneous Principles

3.8.3, 6.2.2, 3.8.4

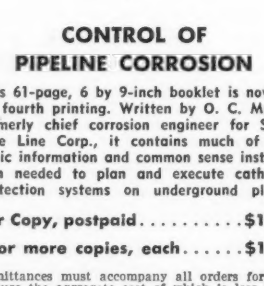
Formation and Properties of Passive Films on Iron. Morris Cohen. Can. J. Chem., **37,** 286-291 (1959).

A unified mechanism for the formation of passive films on iron in aqueous solutions together with the effects of water, oxygen and oxidizing and non-oxidizing ions. The gamma-ferric oxide film is formed first by oxidation of water-formed magnetite, while further thickening of the film occurs by oxidation of diffusing Fe^{++} ion at the water surface of the oxide film. 15 references. —RML. 17770

3.8.3, 3.8.4, 6.3.15, 2.3.9

Study of Anodic Behavior of Titanium. Pt. 2. Characteristics of Protective Films Formed on Titanium. (In Italian.) Bruna Rivolta. Metallurgia Italiana, **50,** No. 7, 255-262 (1958) July.

Oxide films formed during 2-hr. treatments in solutions of hydrochloric acid, sodium chloride, boric acid, potassium hydroxide, sodium monosulfide, sodium fluoride, perchloric acid, sulfuric acid, sodium fluoride plus hydrochloric acid and sodium fluoride plus sulfuric acid at 25, 50 and 65 C and over 8 v. studied by electron diffraction and metallographic microscopy. Diffraction patterns of titanium surfaces chemically treated in solutions of concentrated hydrochloric acid, acqua regia, boiling nitric acid for ½ hr and in nitric acid at ambient temperature for 100 hr. 7 references.—MR. 17588



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3.8.3, 3.6.8, 5.2.1, 6.2.5

Passivity and Corrosion-Resistance of Stainless Steels. N. D. Tomaschov. Paper before International Conf. on Passivity of Metals, Darmstadt, Sept. 2-7, 1957. Z. Elektrochemie, **62,** No. 6/7, 717-729 (1958).

Report of recent Russian investigations on new methods of improving corrosion resistance of metals and alloys amenable to passivation. This may be accomplished by changing their electrochemical potentials in positive direction through anodic polarization, formation of alloys through cathodic process, or formation of thin (not necessarily complete) layer of a noble metal on surface of alloy to be protected. Phenomena occurring during anodic and cathodic polarization of stainless steels in acids (sulfuric acid, hydrochloric acid and nitric acid) were investigated (e.g., transpassivity, anodic protection, negative difference effect, negative and positive effect of cathodic protection). Notes are made on effect of palladium, platinum or copper additions (singly or in pairs) on corrosion behavior of 18-8 in sulfuric acid and in hydrochloric acid. Graphs.—INCO. 17625

3.8.3, 3.6.8, 6.3.15, 4.3.2

Studies of the Anodic Behavior of Titanium. Pt. I. Measurements of Anodic Voltage. (In Italian.) Bruna Rivolta. Metallurgia Italiana, **50,** No. 5, 173-180 (1958).

Rivolta studied the influence of current density and temperature on the anodic behavior of titanium in 0.5N solution of hydrochloric acid, sodium chloride, boric acid, NH_2HSO_3 potassium hydroxide, sodium monosulfide, sodium fluoride and perchloric acid. With sodium fluoride, a study was made of the effect of addition of hydrofluoric acid, hydrochloric acid and sulfuric acid. In all except the F^- solutions, there was electrode passivation, with formation of protective films; particularly high voltages were found for boric acid, NH_2HSO_3 and perchloric acid. The voltage is not much influenced by agitation or aeration, but is usually lowered by increase of temperature. In sodium fluoride solution, the voltage is reduced by addition of acids, the effect being greater in hydrofluoric acid than in sulfuric acid or hydrochloric acid, and the electrodes are considerably corroded; the hydrofluoric acid dissolves the protective film, as is indicated by the fact that, on closing the circuit, the voltage first rises to a maximum and then decreases to a steady value with time, this value being low and not sensitive to current density. 14 references.—MA. 17587

3.8.4, 6.3.8

Oxidation of Liquid Lead. T. F. Archbold and R. E. Grace. Trans. Met. Soc., Am. Inst. Mining & Metallurgical Engrs., **212,** No. 5, 658-659 (1958).

Rate of oxidation of pure (99.999 percent) liquid lead in air was measured at 453-643 C by observing the rate of formation of interference colors on static lead baths, the surface films formed being-up to 730 C — yellow orthorhombic Pb monoxide with the (110) planes parallel to the surface. (Thickness $(X))^2$/time (t) plots show that the exponent n in the relation $X^n = kt$ is ~ 2, leading to the conclusion that the oxidation rate is parabolic for X up to 2000 A, although there may be a tendency for the rate to be slower in the range X = 400-600 A. $k(\times 10^{-5}) = 2.8$, 7.0, 13.3 and 19.5 A^2/min. at 453, 533, 600 and 643 C respectively. 9 references. —MA. 18158

3.8.3

Electron Configuration in Alloys and Passivity. Herbert H. Uhlig. Z. Elektrochem., **61,** No. 6/7, 700-707 (1958).

Passivity in the transition metal alloys occurs at specific critical compositions which appear to be related to d-electron vacancies in the component metals and their tendency to fill with electrons. The d vacancies, measured in part by the magnetic saturation moment, favor formation of strongly chemisorbed surface films, e.g. oxygen, which confer increased resistance to corrosion or passivity by satisfying metal surface affinities.—BTR. 18961

3.8.4

Physical and Chemical Properties of Surfaces. J. M. Honig. Ann. Rev. Phys. Chem., **10,** 77-102 (1959).

Adsorption, chemisorption, catalysis, adsorbent-adsorbate interactions, properties of adsorbed layers and physical properties of surface layers and thin films are reviewed. 290 references.—MA. 19226

3.8.4, 3.5.9

Kinetics of Oxidation in a Gas Stream. J. T. Waber. Amer. Soc. Metals, Conf. on Metals for Supersonic Aircraft and Missiles, **1958,** 96-169. Available from The Society, 7301 Euclid Ave., Cleveland 3, Ohio.

The details of processes, such as diffusion, occurring in oxide films during high-temperature oxidation are considered and the magnitude of temperature and heat fluxes which could result from aerodynamic heating discussed. The effect of forced convection on heat and mass transfer is described. The nature of oxidation reactions and the behavior of various metals with oxygen are outlined. Empirical growth-laws are summarized, and the diffusion process occurring during oxidation described. The influence of lattice defects on migration processes is discussed and illustrated, and typical interfacial reactions given describing the oxidation of metal in terms of the defect concept. The modes of electrical conduction and diffusion are described and the connection between diffusion coefficient and parabolic oxidation-rate constant considered. The oxidation of cobalt, tungsten and zirconium is discussed. The friction and heat transfer as they exist in laminar and turbulent flow are reviewed briefly and enthalpy modifications of the heat-transfer equations discussed. Heat-transfer calculations in aerodynamic research are summarized. 69 references. —MA. 18997

3.8.4

The Oxidation of Metals and Alloys. Final Report for September 1, 1953-December 31, 1958. M. Borcsik and R. J. Borg. James Forrestal Res. Center, 1959, 39 pp. Microfilms and Photocopies Available from Library of Congress, Photoduplication Service, Publication Board Projects, Washington 25, D. C. (PB 142506).

1) The absorption of non-collimated radiation in the experimental measurement of diffusion coefficients by tracer techniques, 2) the plasticity of oxides

and the effect of pores and cracks on the kinetics of oxidation of metals, 3) the role of defects in oxide and sulfide crystals on conductivity, diffusion and scale growth, 4) metal-sulfide equilibria for the lead sulfide-lead, tungsten disulfide-tungsten and Rh_2S_3-Rh pairs, 5) the iron-nickel-oxygen equilibria and the course of the oxidation reaction of iron-nickel alloys, 6) the variation of self-diffusivity in the Curie point of alpha iron. 36 references.—GRR. 19033

3.8.4, 6.3.10, 3.7.4

Diffusion of Aluminum, Magnesium, Silicon, and Zirconium in Nickel. Herbert W. Allison and Harold Samelson. Bell Telephone Labs. J. Applied Phys., 30, 1419-1424 (1959) Sept.

The diffusion rates of aluminum, magnesium, silicon and zirconium, alloyed as single additives in nickel, were measured at temperatures between 800 and 970 C. The method consisted of measuring the weight gain caused by surface oxidation of the additive in a wet hydrogen ambient. The surface oxides were identified by electron diffraction. Grain size was about 0.05 mm in aluminum-nickel, silicon-nickel and magnesium-nickel but less than 10^{-3} mm in zirconium nickel. The composite volume and grain boundary diffusion coefficients are given by $D_{Al \rightarrow Ni} = 1.1 \exp(-59{,}500/RT)$; $D_{Mg \rightarrow Ni} = 2.3 \times 10^{-5} \exp(-31{,}30/RT)$; $D_{Si \rightarrow Ni} = 10.6 \exp(64{,}800/RT)$; $D_{Zr \rightarrow Ni} = 1 \times 10^{-5} \exp(-26{,}700/RT)$. Stereo and photomicrographs indicate considerable grain boundary diffusion, particularly in magnesium-nickel and zirconium-nickel. (auth)—NSA. 19007

3.8.4, 1.2.5, 3.4.9

Chemical Reactions Between Water and Certain Metals at Elevated Temperatures. Paper presented at Joint United Kingdom, United States Canadian Conference on Safety of Reactors, Chalk River, Canada, October 13, 1953. Harry Pearlman. North American Aviation Inc., Special Report Memo-858, January 12, 1954 (Declassified November 6, 1958), 22 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

Thermodynamic data predict that large negative free-energy changes will attend the reaction of water with various metals which are of interest as nuclear reactor materials. Experimental investigations of the reactions have utilized a variety of procedures for initiating reaction: pouring a melt into water; autoclave and other slow methods of heating; exploding metals into water with booster charges; and disrupting metals by passing large electrical currents through them. Although at least some of the available evidence is conflicting, it appears certain that under the proper conditions of initiation explosive chemical reactions can be induced between water and the following metals: aluminum, magnesium, aluminum-uranium alloy (10 percent and 25 percent uranium) uranium, zirconium and aluminum-lithium alloy (3½ percent lithium). Nickel could not be made to react appreciably. These results are in accordance with the thermodynamic data for the schematic reaction: metal plus water equals oxide (or hydrated oxide), plus hydrogen. It appears that explosive chemical reaction with water may occur in thermodynamically favorable cases, either when the metal is initially dispersed into a finely divided state or under certain other circumstances. (auth).—NSA. 18095

4. CORROSIVE ENVIRONMENTS

4.3 Chemicals, Inorganic

4.3.2, 3.4.8, 6.4.2

Effect of the Composition of Corrosive Reagents with or without Copper on the Micrographic Attack of Refined Aluminum. (In French.) Gérard Wyon. Compt. rend, **247,** No. 4, 458-461 (1958) July 28.

Reagents of fluorinated aqua regia can, according to their composition, give rise to two types of attack. One produces corrosive shapes in geometric form and the other produces numerous microfigures. The addition of a few ppm of copper ions changes a reagent giving microfigures to one giving geometric figures only in the case of aluminum of ordinary purity. (auth)—NSA. 18108

4.3.2, 6.2.5, 6.3.15, 6.3.6, 6.3.10

Corrosion of Stainless Steel, Titanium and Titanium Alloys by Ammonia-Base Sulphite Liquor. L. C. Jenness. Paper before TAPPI, 12th Eng. Conf., Cincinnati, 1957. TAPPI, **42,** No. 5, 404-406 (1959) May.

Several types of stainless steel, titanium, titanium alloys, copper-base alloys, Monel and Inconel were subjected to pilot plant corrosion tests in neutral sulfite and ammonia-base acid sulfite liquors. Copper-base alloys (olympic bronze, aluminum bronze, phosphorus bronze, copper-nickel, Monel) and copper itself reduced sulfite to sulfide and thereby corroded rapidly. This corrosion was accelerated by presence of ammonium bisulfite in cooking liquor. Inconel specimens also reduced sulfite liquor and were removed after 44 hrs. exposure with calculated penetration of 0.273 ipy. As result of screening tests, Type 316, two types of titanium metal and two titanium alloys were subjected to acid sulfite liquor under commercial conditions of 24 hrs. for many weeks. All titanium and titanium alloys were superior to Type 316. Iodide titanium exhibited best resistance to corrosion. Photomicrographs indicate some progressive corrosion and widening of attacked area, in case of Type 316 and one titanium alloy. Table gives calculated penetration in ipy.—INCO. 18483

4.3.2, 2.3.9, 6.2.3

Corrosion of Steel in the Presence of H_2S. J. J. Point. Inst. Interuniversitaire des Sciences Nucléaires, Brussels and Faculté Polytechnique de Mons, Belgium. Prepared for the 2nd United Nations Conference on Peaceful Uses of Atomic Energy, A/CONF.15/P/127, 1958, 13 pp. On deposit at the Depository Libraries.

It is known that hydrogen sulfide accelerates steel corrosion. Radioactive tracers were used in this investigation to clarify the mode of action of hydrogen sulfide. Sulfur-35 was used in an investigation of the internal and superficial distributions of sulfur and Tl^{204} for localization of the cathodes. A description is given of the experiment techniques. A study was made of corrosion by hydrogen sulfide in an aqueous deaerated acid medium of mild steels recrystallized at 700 C following critical hardening. The corrosion by gaseous hydrogen sulfide saturated with water of samples under tension and without tension was investigated.—NSA. 18937

4.3.3, 6.2.5, 3.7.2

The Corrosion Characteristics Owing to Uranyl Salt Solution and the Changes of Mechanical Properties of Some Austenitic Stainless Steels. (In Japanese.) Gunji Shinoda, Tadao Sano and Tadashi Kawasaki. Nippon Kinzoku Gakkaishi **22,** 500-503 (1958) Oct.

A study was made to examine the corrosion characteristics caused by

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uranyl salt solution, the effect of mechanical stresses on it, and the effect of corrosion on mechanical properties of some austenitic stainless steel. The results were as follows. 1) After the specimens were heated for 100 hr. at 680 C, carbide precipitation was more pronounced in Type 316 L steel containing molybdenum and copper than the others, while stainless steel containing niobium has shown always a high corrosion resistance. 2) While the tensile strength of the specimens was unaffected by corrosion, a considerable decrease in their yield point and elongation resulted owing to corrosion, and this tendency was more noticeable in the specimens containing molybdenum and copper with the exception of specimen 30A containing niobium. 3) The effect of mechanical stresses on the corrosion characteristics was examined by an auto-radiograph of corroded specimens, and it was found that the stress-corrosion resistance of the specimen containing molybdenum and copper is inferior to that of the specimen containing niobium. The corrosion resistance of niobium stabilized steel appears to be almost unaffected by imposed stresses. It may be reasonable to conclude that molybdenum and copper in stainless steel are unfavorable for corrosion due to uranyl salt solution while niobium is always beneficial to corrosion characteristics of stainless steel. (auth)—NSA. 18952

4.4 Chemicals, Organic

4.4.7, 5.8.1

Performance of Zinc Dithiophosphates as Lubricating Oil Additives. R. Larson. Sci. Lubrication, **10,** 12-16, 18-19 (1958) August.

Although zinc dialkyl-dithiophosphates have been recognized for a number of years as good anti-oxidants in lubricating and motor oils, little research has been done to establish optimum types of compounds for specific purposes. The compounds are discussed in general here, and it is shown that type has a marked effect on solubility, thermal stability, anti-oxidant and anti-wear properties.—ZDA. 18199

4.4.1, 6.3.19, 6.3.2, 1.3

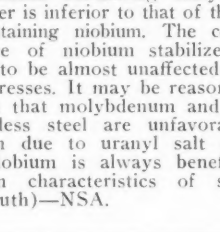
Corrosion of Metals by Vapours from Organic Materials. V. E. Rance and H. G. Cole. Published by Her Majesty's Stationery Office. Admiralty and Ministry of Supply Inter-Service Metallurgical Research Council, 1958, 24 pp.

This survey deals with the corrosion of metals exposed to organic vapors in service and in laboratory tests. Vapors from glue, varnish, paint, plastics and wood are dealt with, and much information is given about the behavior of zinc and cadmium. The booklet concludes with a survey of work in progress.—ZDA. 18930

4.4.7, 8.4.3, 3.4.8

The Corrosion Resistance of Metals in Petroleum Gases Containing Hydrogen Sulfide. (In Russian.) V. M. Nikiforova and N. A. Reshetkina. Metallovedenie i Obrabotka Metallov, No. 5, 55-62 (1957) May.

Attempts to find a corrosion-resistant steel capable of withstanding petroleum gases containing hydrogen sulfide.—BTR. 14748



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4.7 Molten Metals and Fused Compounds

4.7

Liquid Metals for Heating and Cooling. Pt. IV. Frank H. Slade. Machinery Lloyd, European Edition, **30,** No. 17A, 39-43 (1958); **ibid.,** Overseas Edition, No. 19, 70-72, 73-75 (1958).

Sodium and sodium-potassium can be handled at elevated temperatures through pipes of stainless steel, Inconel and Nichrome V, but welded joints may be attacked by sodium. Examples are given of valves, pipework, etc., for handling these liquids at temperatures approaching 815 C.—MA.

4.7, 8.4.5

Solid-Metal-Liquid-Metal Reactions in Bismuth and Sodium. John R. Weeks and David H. Gurinsky. American Society for Metals Seminar on Liquid Metals and Solidification, 1957, **1958,** 106-161; disc., 162-163. Available from the Society, 7301 Euclid Avenue, Cleveland, Ohio.

The work is related to the use of liquid-metal coolants in nuclear reactors. The dissolution and mass transfer of a solid metal by a liquid metal flowing round a cycle with hot and cold sections are described. The effects of oxygen in the melt, dissimilar metals in contact with the melt, and alloying are discussed with examples. The effects of metal additives and inhibitors such as zirconium and titanium in bismuth are described and many results given for the dissolution of iron and steels. The effects of chromium and magnesium are also considered. A thermal-convection loop for studying dynamic corrosion is described in principle, and photographs and radiographs show corrosion in the hot and cold legs. 44 references.—MA. 18999

4.7, 8.4.5, 1.3

Sodium and Bismuth Liquid Metal Fuel Systems: A Literature Search to June 30, 1957. Richard C. Vogel and Walton A. Rodger. Argonne National Lab. U. S. Atomic Energy Commission Pubn., ANL-5933, November, 1958, 54 pp. Available from Office of Technical Service, Washington 25, D. C.

The literature on sodium, sodium-potassium and bismuth liquid metal reactor fuel systems is reviewed to June 30, 1957. The various criteria which have been used for the selection of liquid metal fuel carriers are discussed. Corrosion information on each fuel carrier is summarized, and some discussion of the fabricability of components from possible materials of construction is included. Work done on the testing of various fuel concepts for each carrier is indicated. (auth)—NSA. 18991

4.7, 6.3.6, 6.3.11

The Attack of Solid Alloys by Liquid Metals and Salt Melts. (In English.) J. D. Harrison and C. Wagner. Massachusetts Inst. of Tech. Acta Metallurgica, **7,** 722-735 (1959) Nov.

If one component of a solid alloy is leached out by a liquid metal or salt melt at elevated temperatures, a plane solid-liquid interface is not stable according to a theoretical analysis. Rapidly advancing liquid penetrations were observed in: solid copper-nickel alloys involving 18 to 87 at. percent copper immersed in liquid silver at 1000 C with preferential dissolution of copper; solid gold-copper alloys involving 67 and 74 at. percent gold immersed in liquid bismuth at 400 C with preferential dissolution of gold; and solid silver-gold alloys involving 12 at. percent gold from which silver was dissolved anodically in molten silver chloride at 800 C. In contrast, a plane solid-liquid interface was found when copper-nickel alloys were immersed in liquid bismuth at 800 C since the solubilities of copper and nickel in liquid bismuth are about equal. (auth)—NSA. 19191

4.7, 6.3.10, 6.4.3, 8.4.5

Examination of Sodium, Beryllium, Inconel Pump Loops, Numbers 1 and 2 G. M. Adamson and E. Long. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-54-9-98, September 13, 1954 (Declassified October 9, 1959), 12 pp. Available from Office of Technical Services, Washington, D. C.

From data obtained from two loops, the use of beryllium in Inconel systems containing molten sodium appears feasible if the temperature is held below 1200 F.—NSA. 19030

4.7

Compatibility Tests of Various Materials in Molten Sodium. R. Carlander and E. E. Hoffman. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-57-3-126, March 25, 1957. (Declassified October 9, 1959), 10 pp. Available from Office of Technical Service, Washington, D. C.

Compatibility tests of materials in contact in sodium under 500 psi pressure were conducted for 716 hr. at 1500 F. Of the diffusion couples studied, the Inconel-beryllium system showed the largest amount of alloying. The reaction between molybdenum and beryllium re-

sulted in the formation of two compounds, both of which were severely cracked in several areas. The molybdenum-Inor-8 and the Inor-8-type 316 stainless steel interfaces showed little alloying. A compatibility test system was prepared by placing ¼ x ½ x 1 in. specimens of Inconel, beryllium, molybdenum, Inor-8, and type 316 stainless steel together in sodium.—NSA. 19071

4.7, 6.2.2

Mass-Transport and Corrosion of Iron-Based Alloys in Liquid Metals. G. W. Horsley. Atomic Energy Research Establishment, Harwell, Berks, England. Reactor Technology, **1,** 84-91 (1959) Aug.

The application of mass-transport equations to the corrosion of metals by liquid metals is discussed. Calculated corrosion rates are compared with experimentally determined rates. It is concluded that diffusion controlled solution attack, although significant, may not under conditions of interest to reactor engineers be as serious as either intergranular attack or chemically assisted mass-transport. The mechanism of intergranular attack, the thermodynamics of an example of chemically assisted mass-transport, the role of oxygen in sodium-stainless steel circuits, and methods of reducing mass-transport of iron are discussed. (auth)—NSA. 19225

5. PREVENTIVE MEASURES

5.3 Metallic Coatings

5.3.2, 5.4.2, 6.3.9

Protective Coating Systems for Molybdenum. R. I. Jaffee. pp. 119-133 of "Fabrication of Molybdenum," 1959. American Society for Metals, 7301 Euclid Avenue, Cleveland 3, Ohio.

Application methods, strength, ductility, resistance to thermal shock and protection against oxidation at elevated temperatures of silicide, nickel, chromium and nickel-chromium, aluminum, aluminum-silicon-chromium and ceramic coating systems. 34 references.—RMI. 19248

5.3.2

Chromium Coatings from Liquid Metal Solutions. Peter Schwarzkopk, Ernst B. Weglein and John Wulff. Massachusetts Inst. of Tech., Cambridge. Metals Processing Lab. Contract Nonr-1841(30), December, 1958, 29 pp.

Chromium deposition on molybdenum from liquid tin-chromium baths is discussed. It was found that three types of solid-liquid interface are found to form by continuous cooling of a saturated solution of chromium in tin below the liquidus temperature: these are plane with cubic, with dendritic and with pseudo-dendritic over-growth. The third type of interface is particularly harmful to the protective nature of the coating deposited because of lack of thickness, density and the entrapment of carrier metal. In order to avoid the formation of the pseudo-dendritic interface, further isothermal processing methods were investigated in detail. It was found possible to produce 0.001 in. coatings of chromium which are soft, dense and relatively smooth by an "isothermal technique." Such coatings are too thin to offer protection to molybdenum above about 900 C in air. Since they exhibit solid solution alloy bonding to the substrate and can be laid down to duplicate the contour of machined short-blasted, and otherwise roughened surfaces, the 0.001 in. chromium deposits offer some promise as a barrier substrate for spray coats. (auth)—NSA. 18945

5.3.2

Protective Metallic Coatings. Charles L. Faust. American Society for Metals Conference on Metals for Supersonic Aircraft and Missiles, **1958,** 170-201. Available from the Society, 7301 Euclid Avenue, Cleveland 3, Ohio.

The factors affecting the choice of a suitable coating and methods for applying the coatings are described. The high-temperature properties, including oxidation-resistance, thermal expansion, and stability of some metallic coatings, are outlined and illustrated. The importance of the interfacial zone between the basis metal and its protective coating is discussed. Surface preparation of the basis metal is described and illustrated with photomicrographs. Intermediate coatings are also reviewed and illustrated. Corrosion losses of coatings are considered. 18 references.—MA. 19135

5.3.4

Vacuum-Deposition as a Surface-Finishing Process. W. Reichelt. Metalloberfläche, **12,** No. 9, 278-282 (1958).

A review of some of the technical aspects of commercial vapor-deposition, including suitable metals and alloys, pre-treatment and set-up of the articles to be coated, special methods of evaporation and applications—the production of tarnish- and corrosion-resistant and/or decorative coatings on silver-ware, aluminum and zinc die-castings, and in the canning industry.—MA. 18924

5.3.4, 5.4.2, 6.3.9

Coatings for Protecting Molybdenum from Oxidation at Elevated Temperature. E. S. Bartlett, H. R. Ogden and R. I. Jaffee. Battelle Memorial Inst. March 6, 1959, 43 pp. Available from Office of Technical Services, Washington, D. C. (Order PB 151064).

Coatings that have been developed for protecting molybdenum from oxidation are described, and their protective capabilities discussed. The suitability of the various coatings is dependent upon the anticipated application. Protective coatings are considered from two points of view—the coating system and the method of application of the coating to the molybdenum base. Systems discussed include chromium, silicon, nickel, precious metals, ceramic materials and refractory oxides. Methods of application are electroplating, flame spraying, vapor deposition, cladding, enameling and liquid-phase diffusion. Capabilities of various semicommercial coatings are compared in a very general manner. The results of a number of service tests on coated molybdenum parts are summarized. These include investigations of materials for potential use as jet-engine turbine buckets, nozzle vanes, thermocouple protection tubes, ramjet flameholder gutters, pitot tubes, glass-bath electrodes and glass-bath stirring rods. (auth)—NSA. 19003

5.3.4

Galvanized Sheet for Outdoor Applications. M. H. Davies. Metal Finishing J., **5,** No. 51, 98-100 (1959) March.

This article describes the classes of continuously galvanized strip and sheet, plain and corrugated, available under B.S. 3083 and B.S. 2989, and the life that may be expected from them under various conditions. The advantages to

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be gained by painting galvanized sheet under certain conditions are also discussed.—RPI. 19115

5.3.4

Vacuum-Evaporated Cadmium Deposits. D. J. Fishlock. Electroplating and Metal Finishing, **12,** No. 6, 221-222, 224 (1959) June.

Cadmium is evaporated by resistance heating in a vacuum chamber at 5×10^{-4} mm mercury. Deposition rate is high owing to the high evaporation rate and low boiling point of liquid cadmium at this low pressure. Specimens are degreased and sandblasted before coating; they show no loss of ductility as a result of coating, whereas electroplated cadmium has a severe embrittlnig effect on steel. Adhesion is purely mechanical but is about that of electrodeposited cadmium.—MA. 19122

5.3.4

Definition of Electrodeposition Baths. (In French.) J. Glayman. Corrosion et Anticorrosion, **7,** No. 6, 265-268 (1959).

Glayman remarks on the lack of definitions of bath characteristics, and calls for amplification by suitable statements on composition, practice, impurities and their elimination, etc. Characteristics of the deposits are also considered.—MA. 19172

5.3.4

Hot Galvanizing. R. Haarmann. Corrosion et Anticorrosion, **7,** No. 4, 146-152 (1959). (In French.)

Processes are outlined and statistics of zinc consumption are presented. Corrosion behaviors and weight-losses of the coatings under various conditions are discussed and the combination of galvanizing and painting is considered. —MA. 19188

5.3.4, 6.2.2

Hot-Dip Tinning of Cast Iron. Ernest S. Hedges. Giesserei, **46,** No. 9, 233-236 (1959).

The fused-nitrate or the direct-chloride processes, which are described and compared with other processes, of chemical oxidation of the surface graphites in both lamellar and nodular castings produce brilliant tin coatings on cast-iron surfaces. For bearing-bases, the direct-chloride process gives a very strong, adhesive coating and increases the adhesive strength between the bearing metal and the iron casting.—MA. 19200

5.4 Non-Metallic Coatings and Paints

5.4.2, 6.6.4

Coating of Graphite with Silicon Carbide by Reaction with Vapor of Controlled Silicon Activity. John M. Blocher, Jr., Don P. Leiter, Jr., and Robert P. Jones. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-1349, June 15, 1959, 17 pp. Available from Office of Technical Services, Washington, D. C.

In the reaction of silicon halides with graphite to form silicon carbide, thermodynamic conditions were determined for the formation of silicon carbide, free of elemental silicon. The use of these conditions was designed to limit the rate of coating formation by the rate of diffusion of carbon through the coating, and render the operation independent of the vapor-flow factors which normally limit the uniformity of vapor-deposited coatings. Although a wide range of pressure-temperature-composition conditions was explored, it was not possible to duplicate the success previously obtained in applying the method to niobium carbide, tantalum carbide, titanium carbide and zirconium carbide coatings. Fundamental differences in the characteristics of the carbides which may account for the defference in behavior are the lack of a range of homogeneity in beta silicon carbide crystal structure, and the fact that silicon carbide undergoes a modification from the cubic beta to a hexagonal form at 1900 to 2000 C. There remains the prospect of forming a uniform SiC "sponge" by the present process which can be subsequently impregnated with metallic Si to form an oxidation-resistant coating. (auth)—NSA. 19049

5.4.5

Multicolor Coatings for Corrosion Protection. N. I. Gaynes. Metal Finishing, **57,** No. 9, 73-76 (1959) Sept.

Multicolor paints are made possible by suspending lacquer enamel vehicle in aqueous stabilizing medium. Carrier solution places protective colloidal envelope around each particle so that merging of colors is prevented. Colloidal solution evaporates, allowing aggregates to flow together as film. Multicolor paints provide film thicker than that obtained from conventional paints. For steel surfaces pretreatments such as phosphating and priming are required for maximum corrosion resistance and extended film life. Tests made with various primers (alkyd, zinc chromate, polyvinyl alcohol) under multicolor paints are discussed. These include industrial and salt atmosphere outdoor exposure tests of wood panels, and laboratory salt spray test of phosphated steel panels.—INCO. 19163

5.4.5, 8.9.1, 6.4.4

Organic Protection Schemes for Modern Helicopters. P. W. Hyde. Electroplating, **12,** No. 7, 249-254 (1959.)

The protection of helicopters from corrosion is a specially difficult problem, particularly when considerable quantities of magnesium alloys are incorporated. The scheme developed for an anti-submarine helicopter, about to come into service, comprises two coats of stoved epoxy resin on all magnesium alloy sheet, forgings and castings, while the whole aircraft, including magnesium steel and aluminum alloys, is finished with one further coat of epoxy primer and a finishing coat of catalyzed epoxy air-drying paint. Tests over a period of several years have shown that this system is far superior to anything used previously and, in particular, that it is now possible to use magnesium alloy components safely in conditions of continuous sea water mist corrosion. The large steel-framed helicopter is shot blasted and zinc is sprayed on before applying the epoxy paint scheme.—RPI. 19233

5.4.5

Coal-Tar Epoxides. P. J. Ashby. Corrosion Prevention and Control, **6,** 50-51 (1959) Sept.

Protection of chemical industry and marine equipment by coating with a combination of epoxide resins and coal tars. Advantages of coatings.—RML. 19004

5.4.5, 8.9.5

Nonmetallic Coatings for Protecting the Tanks in Tankers Against Corrosion. V. A. Bershtein and B. L. Krasil'shchikova Sudostroenie (Shipbuilding), No. 3, 38-42 (1959). (In Russian.)

An evaluation of oilfree paint and varnish coatings in tanker cargo compartments for protection against attack by petroleum products and sea water showed that epoxide resin-based coatings have best resistance. Also investigated were aluminum paint and ethynol varnish with aluminum powder or iron oxide, bakelite varnish with 20-25 per cent aluminum powder and various primers, enamels and varnishes. The compartments used, rarely, if ever carried water ballast. 19031

5.4.5

Influence of the Nature of the Basis Metal on the Adhesion of Anti-Corrosive Paints. (In Italian.) A. Turco. Galvanotecnica, **9,** No. 11, 280-281 (1958); Metal Finishing Absts., **1,** No. 1, 29 (1959).

The properties of lead- and zinc-based primers are briefly reviewed with reference to adhesion on steel, copper and light alloys. The ideal primer has optimum adhesion and impermeability irrespective of humidity, good chemical resistance, inhibiting action, elasticity and plasticity and resistance to abrasion and to thermal shock and is non-toxic.—RPI. 19053

5.4.5

Experiences with Amine Hardened Epoxy Resin Coatings in Industry and Marine Transportation. (In German.) A. J. Wildschut. Werkstoffe u. Korrosion, **9,** No. 12, 741-746 (1958).

Amine-hardened epoxy resin coatings have been used for corrosion prevention in the chemical industry, in refinery installations, in storage tanks and in ocean tankers. The coatings protect metals and concrete against the action of sea water, alkaline and acid solutions and oil products. 18981

5.4.5

New Protective Paint Based on Lead Suboxide. V. Novak. Zaštita Materijala, **6,** No. 9, 361-362 (1958).

A new protective paint based on lead suboxide which gives lasting protection to metals and other materials. 80 per cent of the lead suboxide particles are of the size 1-3 μ, so they give a uniform protective layer. The small particles give a lasting suspension in the medium. The covering power is 10 m^2/kg.—RPI. 18908

5.4.8

Anticorrosive Paints for High Temperatures. W. F. Pauk. Chem. Rundschau (Solothurn), **11,** No. 5, 297-299 (1958).

Coatings for high-temperature use are reviewed. Silicone/aluminum paints can be used for temperatures in the region of 750 and a more recent development is a sodium silicate/metal powder coating, where the metal may be bright steel, nickel, chromium or copper.—RPI. 18906

5.4.10

The Use of Plasticized PVC Tapes for the Prevention of Pipe Corrosion. J. S. Gerrard. Pipes and Pipelines, **3,** No. 12, 30-32 (1958) Dec.

Pressure-sensitive polyvinylchloride tape used to prevent pipe corrosion is readily applied even under freezing conditions, conforms to irregular shapes, and is equivalent to asphalt or coal tar

coatings when covered with a protective outer wrap. It is especially suitable for wrapping the ends of stored pipes and for joints in pipelines. 19181

5.4.10, 8.9.3

Protection of Trunk Pipelines Against Corrosion. (In Russian.) V. S. Turkin. Stroitel. Predpriyatii Neft. Prom. (Building Enterprises of the Petroleum Industry), No. 5, 5-8 (1958).

Bituminous coatings used for protecting pipelines against corrosion show improved plasticity and resistance to freezing, without loss of strength, when 0.1-0.2 percent polyisobutylene or natural rubber is added. Addition of 1-3 percent polystyrene increases resistance to alkalis, and 0.3-0.5 percent of an antiseptic agent prevents bacterial breakdown. Ground rubber in the amount of 8-10 percent raises the softening point and improves the physical properties. For bituminous coatings with kaolin as filler the upper limit of protective potential is 1-1.2v., and with rubber it may be raised to 1.5v. In the vicinity of electric railway lines, protection against stray currents is provided by polarized drainage units of 150-500 amp. The production of glass fabric as a wrapper and of polyvinylchloride and polyethylene coatings is being developed. 18963

5.7.8, 5.3.4

The Use of Sequestering Agents in Metal Cleaning and Deposition. R. L. Smith. Metal Finishing J., **4,** No. 47, 429-431 (1958).

Sequestering agents such as citric, gluconic, oxalic and tartaric acids and EDTA are used in metal cleaning, derusting and etching. In plating solutions sequestrants such as EDTA can be used for inactivating impurities but care must still be taken to exclude these. Iron, zinc-tin alloys, copper and gold can be electroplated and copper and nickel chemically plated, from chelate baths. 14 references.—MA. 18960

5.8 Inhibitors and Passivators

5.8.1

Corrosion Inhibitors. (In Russian.) I. L. Rozenfel'd (Rosenfel'd) and V. P. Persyanceva. Kim. Nauka i Promyshlennost' (Chemical Science and Industry), **3,** No. 4, 500-505 (1958).

The mechanism of inhibitor reaction is considered for acid and alkaline solutions. Types of inhibitors, including vapor-phase inhibitors, are reviewed. 43 references.—MA. 18928

5.8.1, 3.3.3, 2.2.7

Harbor Screening Tests of Marine Borer Inhibitors. Pt. I. Tech. Rept. 027; (AD-209527). Harry Hochman and Thorndyke Roe, Jr. Naval Civil Engineering Lab., Port Hueneme, Calif. July 9, 1959, 37 pp. Order PB 143053 from Library of Congress, Photoduplication Service, Publications Board Project, Washington 25, D.C.

This report lists the results of harbor tests of treated panels exposed and removed between September 1955 and August 1958. It also lists all treated panels which have been exposed for one year or more and which have shown no attack or very slight amounts of attack. Heavy metal organic compounds when mixed with creosote, coal tar, or creosote-coal tar solutions are showing very good resistance to borer attack.—GRR. 19217

5.8.4, 8.4.3

Use of High-Molecular Fatty Amines as Corrosion Inhibitors. (In Japanese.) K. Ogasawara. Shoseki Giho (Showa Oil Co. Technical Rev.) **2,** 138-142 (1958); Chem. Absts., **53,** No. 7, 6587 (1959) April 10.

n-Hexadecylamine with linoleic acid in the form of an amide/acid mixture was used as corrosion inhibitor in a petroleum refinery. A mixture of 70 per cent hexadecylamine, 5 percent C_{12}-and C_{14}-amines, and 25 percent C_{18}-amine could be used instead of the pure C_{16}-amine. Up to 2.5 percent emulsifier was added. 18916

5.9 Surface Treatment

5.9.1.

The Preparation of Metals for Protective Finishes. R. E. Shaw. Metallurgical Reviews, **3,** No. 12, 327-356 (1958).

This is a comprehensive review of the subject containing many references to the literature. The author discusses the effect of millscale on iron and steel and its removal by mechanical methods, pickling, surface washes and flame-cleaning. The merits and applications of each method are described. The writer goes on to discuss steam-cleaning, degreasing, derusting and phosphate coatings, and mentions the remarkable increase in the use of the last-named due to the adoption of zinc phosphate, and its adaptability to mass-production conditions. The cleaning of aluminum, copper, stainless steel and tin is also described. The last two sections are devoted to the cleaning and painting of zinc surfaces. 7 illustrations, 4 tables.—ZDA. 18959

5.9.2, 6.3.15

Descaling of Titanium. W. B. Stephenson, Jr. Metal Progress, **73,** No. 3, 87-89 (1958).

Pickling of titanium for 5 minutes in a hot solution of calcium fluoride in sulfuric acid followed by rinsing for 2 minutes in nitric acid 10-hydrochloric acid 2 percent gives a bright surface free from pits. The technique does not cause hydrogen embrittlement or stress-corrosion.—MA. 18974

5.9.2, 6.3.15

How to Avoid Hydrogen Pickup in Descaling Titanium Alloys. Q. D. Wheatley. Metal Progress, **74,** No. 6, 112-113 (1958) Dec.

Short immersion time in titania-modified hydride bath considered necessary; optimum conditions for descaling hydrogen sensitive 5 aluminum-2.5 tin titanium alloy are obtained with molten caustic bath, containing 0.4 to 0.6 percent sodium hydride, 0.35 percent titanium dioxide and 10 to 20 percent sodium carbonate; treatment time should be 30 to 60 sec. at 610 to 645 F.—BL. 18985

5.9.2, 5.3.4

The Preparation of Metals for Electroplating. J. J. Dale and I. J. Howell. J. Australian Inst. Metals, **4,** No. 1, 27-34 (1959).

The importance of basis-metal preparation in affecting quality and performance of electroplated coatings is stressed. The dependence of adhesion on the surface condition of the basis metal is discussed. The surface condition is affected by its mechanical history, and by the chemical and electrochemical effects of cleaning and etching. The last two methods of improvement are discussed in detail. 26 references.—MA. 19097

5.9.4

Present Practice in Anodizing, G. Elssner. Aluminum, **35,** No. 7, 374-382 (1959).

After a short historical review, Elssner discusses modern techniques in anodizing and modifications to meet special requirements. The mechanism of film formation is described, with methods of determining film thickness and notes on sealing and coloring. Modern anodizing equipment is illustrated, including that for hard anodizing etc.—MA. 19109

5.9.4

Recent Developments in Phosphate Treatments. H. A. Holden. Product Finishing, **12,** No. 1, 76-79 (1959).

Advances in phosphate treatment are reviewed. Emphasis is given to the new low-temperature processes and the so-called "light-weight" processes based on sodium and ammonium phosphates.—MA. 19222

5.9.4, 3.8.4

A theory on the Complementing Process in Phosphating Baths. (Formation Rate of Secondary Cover Layers on Metals). (In German.) W. Jaenicke and B. Lorenz. Werkstoffe u. Korrosion, **10,** No. 12 (Supp.), 761-767 (1959) Dec.

Secondary cover layers are deposited on metal from saturated solutions if the equilibrium of the solution is disturbed by corrosion on the metal surface. The rate of corrosion and the rate at which the layer is formed are compared, using the phosphate treatment of iron as an example. With this process, the quotient of the H^+ consumed and the iron dissolved is governed by the stoichiometry of the oxidation reaction concerned. The quotient of the H^+ consumed and the quantity of the zinc phosphate deposit can be calculated if all reactions are diffusion controlled. It is thus assumed that the crystal nuclei are formed rapidly and that equilibria between zinc and phosphoric acid in the solution remain adjusted up to the metal surface. This theory is confirmed experimentally. It serves to indicate baths with optimum properties and to determine the composition of complementary solutions by means of which the baths can be kept stable. 19249

6. MATERIALS OF CONSTRUCTION

6.2 Ferrous Metals and Alloys

6.2.2, 4.3.2

Cast Iron and Fuming Sulphuric Acid. (In German.) J. Beran Werkstoffe u. Korrosion, **10,** No. 11, 665-666 (1959) Nov.

It is well known that the chemical industry is using cast iron reaction chambers for fuming sulfuric acid, although this practice is described as impermissible in the technical literature on corrosion. A scrutiny of the literature shows that this proscription dates back to two early publications which were concerned with a cast iron material in no way comparable to modern cast iron. It is essential to keep the dangerous silicon content low, and this is in fact being taken into account with modern

cast iron by the suitable proportioning of carbon and by the heat treatment. 19046

6.2.2, 3.8.4, 4.6.2

Kinetic Studies on the Iron-Steam Reaction. (In Italian.) B. Brigoli, E. Cerrai, A. Scaroni and M. Silverstri. Energia nucleare (Milan), **6,** 330-338 (1959) May.

Iron containing porous material was prepared to determine its chemical and mechanical behavior during the steam-iron hydrogen-producing reaction. Materials containing about 50 to 90 per cent iron in aluminum oxide were prepared, and their mechanical behavior tested. The 90 per cent iron product was used for kinetic studies on the oxidation and reduction reaction rates. Results are reported and experimental equipment is described. (auth)—NSA. 19051

6.2.2, 5.8.4, 5.2.1

Simultaneous Action of Organic Inhibitors and Cathodic Polarization on the Corrosion of Iron. L. I. Antropov J. Sci. & Ind. Res., **18B,** 314-319 (1959) Aug.

Calculation of increase in cathodic protection of metals, particularly iron, by alteration of anodic and cathodic polarization. Data show a decrease in corrosion rate when electric current is applied to organic inhibitors in solutions.—RML. 19020

6.2.2

New Wrought Iron has Better Corrosion Resistance. E. P. Best. Materials in Design Eng., **49,** No. 2, 100-102 (1959) Feb.

Improved corrosion resistance, about 25 per cent better than previous grade, of new 4-D wrought iron, introduced by A. M. Byers Co. is due to increased deoxidation of base metal, together with increase in phosphorus content and change in composition of iron silicate; properties of new material which shows its greatest advantage over carbon steels in heat transfer equipment handling brines, industrial cooling waters, etc; it is unaffected by refrigerating gases such as ammonia, carbon dioxide and Freon.—BL. 19036

6.2.2, 3.2.3

Further Studies on the Metallurgy of Silicon Iron. Some Observations on Selected Oxidation. A. U. Seybolt and E. I. Alessandrini. General Electric Research Lab., Schenectady, N. Y. Trans. Met. Soc. AIME, **212,** 507-509 (1958) Aug.

Selective oxidation (preferential oxidation of a single alloy component) can be an important oxidation mode in the case of alloys such as silicon-iron, aluminum-iron, and so on, when heat-treating in atmospheres of low oxygen potentials. It was the purpose of this work to identify the oxide films formed on iron containing 3¼ per cent silicon at low oxygen potentials, and to make some observations on the water/hydrogen ratios required to form them. (auth)—NSA. 18949.

6.2.4, 4.2.5, 4.6.11

Results of Marine Corrosion Tests on 4% Chromium Steels. (In French.) E. Herzog. Corrosion et Anticorrosion, **7,** 312-316 (1959) Sept.

Weight loss and depth of corrosion of specimens containing slight additions of nickel or aluminum. Conditions included exposure to marine atmosphere, immersion in sea water, various types of surface preparation and heat treatment and asphalt painting of surfaces. 6 references.—RML. 19202

6.2.5, 3.7.2, 3.7.3, 4.3.2

Study on 17 Chromium-4 Nickel-4 Copper Stainless Steel. 1st Report: Effect of Copper, Carbon and Nitrogen on Properties of the Steel as Cast. M. Okamoto and S. Kada. Paper before Japan Inst. Met., April, 1958. J. Japan Inst. Met., **22,** No. 7, 363-367 (1958) July.

Effect of copper, carbon and nitrogen on the phase change, aging, mechanical properties and corrosion resistance of 17 chromium-4 nickel-4 copper cast stainless steel. Alloying elements such as copper, carbon and nitrogen lower Ms point of the steel. The amount of retained austenite is increased by these elements after the solution treatment, wherein the effect of carbon is most potent, nitrogen is rather effective and copper is slightly effective. An optimum aging for the maximum hardness would be to heat the steel at 440 C for 3 hours or 480 C for 1 hour after the solution treatment. Aging develops martensite but minimizes austenite. The effect of copper on hardness is maximum when its content is 4 percent. In subzero treatment to transform austenite into martensite, nitrogen-containing retained austenite is more stable than carbon-containing retained austenite. Subzero treatment at —72 C is most effective for martensitic transformation. Tensile strength increases with increase of copper content. Maximum elongation can be obtained by an addition of 2 percent copper. Corrosion resistance in sulfuric acid is remarkably improved by an addition of copper. Corrosion resistance in nitric acid is excellent irrespective to copper, carbon and nitrogen contents of the steel. The best corrosion resistance can be obtained by the solution treatment prior to quenching at 1000 C and followed by an aging at 440 C for 3 hours. An assumption is made, therefore, that the aging may result in strain hardening rather than in precipitation hardening of the steel.—INCO. 18902

6.2.5, 3.7.2, 3.7.3, 4.3.2

Study on 17 Chromium-4 Nickel-4 Copper Type Stainless Steel. 2nd Report. Effect of Nickel, Copper and Nitrogen on Properties of the Steel Cold-Rolled. M. Okamoto, R. Tanaka and A. Sato. Paper before Japan Inst. Met., April, 1958. J. Japan Inst. Met., **22,** No. 10, 504-508 (1958) Oct.

Ms temperature of steel is lowered with increase of nickel, copper or nitrogen contents, thus increasing retained austenite. Precipitation-hardening of the steel is promoted with decrease of nickel content or increase of copper content. Cold-rolling promotes the precipitation-hardening of the steel, thus increasing the hardness. The steel containing nitrogen was hardened remarkably by rolling and aging. It might be due to the high degree of work-hardening and the precipitation of nitride from martensite in the copper-rich solid solution. Corrosion resistance of the steel in a boiling 5 percent sulfuric acid solution is improved as copper and nickel contents increase. The solution quenched steel at 1000 C followed by cold-rolling and subsequently tempered below 440 C does not degrade its corrosion resistance, not like 17-7 and 18-8 stainless steels. Best result can be obtained from steel with composition 17 chromium-4 nickel-4 copper-0.17 nitrogen.—INCO. 18903

6.2.5, 3.5.8, 3.7.2

Some Metallurgical Factors Affecting Stress Corrosion Cracking of Austenitic Stainless Steels. H. H. Uhlig and R. A. White. Corrosion Lab., Massachusetts Inst. of Tech., Cambridge, 1958, 28 pp.

Tests of 18-8 stainless steels in boiling 42 percent magnesium chloride show that alloys with 0.015 percent carbon or 0.01 percent nitrogen or less do not fail at 200 to 260 hours. Commercial 304 alloys fail in 0.2 to 1.4 hr. Stable austenitic steels (20 percent chromium, 20 percent nickel) are similarly resistant if nitrogen content is below 0.002 percent. Carbon confers resistance to cracking in 304 stainless steels. The action of titanium, niobium, silicon, cobalt and boron is also discussed. A mechanism is offered.—NSA. 18965

6.2.5, 3.7.2

How Boron Affects Corrosion of Type 304 Stainless. J. W. Farrell and P. C. Rosenthal. Metal Progress, **77,** 101-103 (1960) Feb.

The protection which boron gives Type 304 stainless steel against corrosion is not outstanding by present standards. Small additions of boron are useful for this purpose in the cast form of stainless steel but prove inadequate when used in the wrought steel.—RML. 19139

6.2.5, 6.3.10, 4.3.2

Stainless Steels and Nickel-Containing Alloys in the Chemical Industry. J. Hinde. J. Australian Inst. Metals, **4,** 103-113 (1959) Aug.

Use of nickel, certain high-nickel alloys and the austenitic chromium-nickel stainless steels. Behavior in nitric acid and sulfuric acid applications. 29 references.—RML. 19214

6.2.5, 4.3.3, 3.5.8, 8.4.5

Corrosion Resistance of CD4MCu Stainless Steel in Reactor-Related Environments. D. N. Hess, R. S. Greeley, P. D. Neumann and J. C. Griess. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-59-11-114, November 30, 1959, 12 pp. Available from Office of Technical Services, Washington, D. C.

CD4MCu steel, either as cast or in the rolled and heat-treated condition, is as resistant to corrosion in uranyl sulfate solutions as cast or wrought type 347 stainless steel under either static or dynamic conditions at temperatures as high as 300 C. Furthermore, CD4MCu appears to be more resistant to stress-corrosion cracking in most chloride-containing environments than type 347 stainless steel. Further testing of this alloy in experimental engineering equipment is recommended. (auth)—NSA. 19229

6.3 Non-Ferrous Metals and Alloys—Heavy

6.3.3, 3.7.2

Oxidation Resistance of Binary Chromium-Base Alloys. E. P. Abrahamson and N. J. Grant. Pages 501-509 of "High Temperature Materials". Book, 1959, John Wiley & Sons, Inc., New York 16, New York.

Study of chromium alloyed with elements in groups IV_A, V_A, VI_A, VII_A and VIII. All elements investigated, with the exception of iridium, cause an initial increase in oxidation resistance of chromium.—RML. 18260

6.3.5, 5.3.4, 3.5.9

Research for Coatings for Protection of Niobium Against Oxidation at Elevated Temperatures. E. C. Hirakis. Horizons Inc. U. S. Wright Air Development Center, U. S. Air Force, February, 1959, 74 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 151684).

Oxidation rate of niobium at 2000 F was reduced by a factor of 20 by additions of cerium, chromium, titanium and aluminum. In addition, flame spraying and electrodeposited coatings were developed which give niobium 4 to 6 hours protection at 2500 F. These efforts to protect niobium against oxidation by alloying and by metallizing or electroplating resulted in the fabrication of test pieces which reportedly show promise and demonstrate the feasibility of the methods employed. Although the arc-melted alloy was superior to pure niobium in oxidation resistance, the degree of improvement fell far short of the factor of 100 which is generally agreed to be the prerequisite for niobium base materials at 2000 F. Specimens produced by the two coating methods equalled or surpassed the minimum standard. However, in their present state of development, both coatings are termed unreliable due to difficulties encountered in reproducing the test results. Preparations, test procedures, and results are described for both the alloy development and coating work.—OTS. 18461

6.3.5, 3.4.6, 2.3.9, 2.3.6

Oxidation of Niobium. Technical Note No. 1 for April 1, 1958 to March 31, 1959. Tor Hurlen, Hallstein Kjöllesdal, Joar Markali and Nico Norman. April, 1959, 126 pp. Contract AF61(052)-90. Available from Central Inst. for Industrial Research, Blindern, Oslo, Norway.

The reaction of niobium with oxygen of pressures from 760 to 10^{-2} torr and temperatures from 150 to 1000 C was studied by means of rate measurements and X-ray diffraction, electron microscopy, and metallographic investigations. (auth)—NSA. 19234

6.3.6, 3.7.2

Corrosion Resistance of Aluminum Bronzes. G. Fitzgerald-Lee. Corrosion Technology, **6,** No. 9, 263-266, 284 (1959) Sept.

Discusses improvement in corrosion-resisting properties of bronzes by addition of aluminum, and covers the following: Acid resistance; process of dealuminification; other alloying additions, notably nickel; atmospheric corrosion; sea water corrosion; impingement and cavitation erosion; pitting resistance; heat treatment effects; aluminum oxide surface films; and resistance to various gases. Tables summarize corrosion data in aerated solutions of dilute acids, ammonia, various chlorides, sodium hydroxide, sea water; cavitation erosion data are also given.—INCO. 19121

6.3.6, 8.3.5

Corrosion of Brass in Aqueous Solutions of Tamarind, Kokum and Hog Plums. M. N. Desai, A. M. Trivedi and J. D. Talati. Indian J. Applied Chem., **22,** No. 2, 45-52 (1959).

Brass vessels used extensively in India for domestic purposes are subjected to corrosion by foodstuffs including the three mentioned souring substances. Corrosive effects were compiled from three-day tests of brass in contact with various concentrated aqueous solutions. Kokum is highly corrosive, while tamarind and hog plum are mildly corrosive. Dezincification of brass is maximum in hog plum and minimum in tamarind. 9 references.—RML. 19077

6.3.6

Copper Corrosion and Its Consequences. J. K. Aiken. Product Finishing, **12,** 90-92 (1959) October.

Corrosion of copper by aqueous solutions and organic compounds. Corrosion inhibiting properties of benzotriazole and related compounds. Accelerating effect of copper dissolved in various liquids on the rate they corrode aluminum or steel. 4 references.—RML. 19014

6.3.6, 8.8.5, 1.3

Copper and Copper Alloys: A Survey of Technical Progress During 1957. E. Voce. Metallurgia, **57,** No. 339, 3-15 (1958).

A survey of work in extraction metallurgy, foundry practice, fabrication, plating and finishing, corrosion, joining, powder metallurgy, physical metallurgy, mechanical properties, testing and analysis. 309 references.—MA. 18984

6.3.6, 3.8.2, 3.6.8

Electrochemical Behavior of Copper. Pt. I. Behavior of Polycrystalline Electrodes. (In Italian.) Guido Poli and Lucia Paganini. Ann. chim. (Rome), **48,** 407-421 (1958).

The electrodes were prepared by electrodeposition on to copper sheet. Overvoltages were determined in sulfuric acid, perchloric acid and sodium sulfate and NH_2HSO_3, alone and with their sodium salts. The anode potential rises to a maximum and then decreases, but the cathode potential shows a maximum only at c.d. > 5 amp/m^2; above this value the maximum is followed by a slight fall and then a steady rise. The overvoltage at both electrodes increases with sulfuric acid concentration (0.1N-N) and on addition of 0.1 N-sodium sulfate, but is scarcely affected by perchloric acid concentration or addition of $NaClO_4$. The effect with $NH_2 \cdot HSO_3$ is similar to, but rather less than, that with sulfuric acid; considerable dissolution of copper occurs. The results indicate inhibition by So_4^{2-} and $NH_2SO_3^-$—MA. 19021

6.3.6, 3.7.4, 3.7.3

The Properties of a New Type of Aluminium Bronze Containing Manganese. (In Italian.) C. Panseri and M. Leoni. Alluminio, **27,** No. 11, 481-493 (1958).

The alloy studied contained copper 75, manganese 12, aluminum 8, iron 3, nickel 2 percent. The microstructure was examined after annealing at temperatures from 100 to 950 C, and comparisons made with a ternary alloy containing copper 80, manganese 12, aluminum 8 percent; at temperatures > 800 C, β was found with small crystals of $FeAl_3$; at 800 C, plates of α began to separate, its amount increasing as the temperature was decreased; at 550 C, NiAl was observed inside the α phase, and β began to transform into $\alpha + Cu_3Mn_2Al + NiAl$. This bronze has a high U.T.S. and a good resistance to erosion. It resists corrosion by air-free dilute sulfuric acid solution and sea water. 18 references.—MA. 18911

6.3.6, 3.5.8, 3.5.3, 3.7.4

Intergranular Cavitation in Stressed Copper-Nickel Alloys. B. J. Reid and J. N. Greenwood. Trans. Am. Inst. Mining & Met. Engrs. (Met. Soc.), **212,** 503-507 (1958).

Present work confirms conclusion reached previously that formation of approximately spherical cavities in grain boundaries during tensile deformation leads to intercrystalline cracking. In cases of copper and α-brass this was always accompanied by a reduction of ductility. New factor found in alloys of nickel with copper (ranging from pure OFHC copper to 43.7 at.-percent nickel) was recovery of ductility at temperatures above 400 C even though cavitation already has commenced. For example, 20 percent alloy at 525 C shows cavitation at 5 percent extension, yet does not fracture until 37 percent. A continuation of original slope of curve (elongation to fracture at various temperatures) would lead to an expectation of fracture after 10 percent extension. Cessation of intercrystalline cracking under these circumstances coincides with appearance of serrations in grain boundaries. It is evident that such a condition must effectively stop grain translation and resultant formation of vacancies leading to cavities. Main observations of experimental work are summarized. Number and size of cavities (in general) increases with nickel content up to 20 percent and then falls off markedly. Cavitation becomes visible at a higher temperature and grain-boundary migration appears at higher temperatures the higher the nickel content.—INCO. 18927

6.3.9, 8.8.5

Consolidation of Molybdenum by Powder-Metallurgy Practice. Howard Scott, W. A. Taebel and D. D. Lawthers. pp. 51-79 of "The Metal Molybdenum," Book, 1958, 696 pp. Available from the American Society for Metals, 7301 Euclid Avenue, Cleveland 3, Ohio.

The problem of contamination of molybdenum powder, chiefly by oxygen and water vapor, is discussed, and the production of pure molybdenum for powder techniques described. Oxidation of pure metal strip at temperatures below 250 C is negligible, but fine powder absorbs oxygen from air at room temperature, the rate decreasing with time but continuing for at least a month. Mechanical properties of sintered molybdenum are discussed and tensile fracture surfaces of annealed molybdenum illustrated. The production and properties of molybdenum alloy powders are described and a vacuum induction-furnace used for sintering molybdenum-base alloy compacts is illustrated. Preferred orientation, the ductile → brittle fracture transition, yield strength, work-hardened, and recrystallization characteristics are discussed. In a commentary by Earl A. Gulbransen the surface reactions of molybdenum are amplified.—MA. 19023

6.3.9

Molybdenum, Its Alloys and Its Protection. Julius J. Harwood and M. Semchyshen. American Inst. Mining and Metallurgical Engrs. Conf. on High-Temperature Materials, 1957, **1959,** 243-272. Available from the Institute, 29 W. 39th St., New York 18, N. Y.

The properties of molybdenum are reviewed, and tables and graphs are given of data on: Compression-creep properties at 1600 F of molybdenum and 4 high-temperature alloys, tensile strength versus temperature of molyb-

denum and molybdenum-0.5 percent titanium, stress-rupture properties of molybdenum and its alloys, 30-sec rupture strength of molybdenum and other pure metals, solubility of various elements in molybdenum, hardness of arc-cast molybdenum, hardness of molybdenum alloys and effects of various elements on molybdenum hardness. Other topics discussed are: Hardness and workability, recrystallization behavior, tensile properties, transition-temperature characteristics, creep-rupture properties, molybdenum-rhenium alloys, oxidation and protective coatings and weldability. 10 references.—NSA. 19196

6.3.10, 4.6.1, 3.7.3, 3.2.2

Corrosion of Inconel in 600 F Static Water. G. E. Galonian and H. L. Tymchyn. Knolls Atomic Power Lab. U. S. Atomic Energy Commission Pubn., KAPL-2047, May 4, 1959, 22 pp. Available from Office of Technical Services, Washington, D. C.

A series of static autoclave tests was made to establish the corrosion rate of Inconel in various waters at 600 F and to determine its resistance to intergranular corrosion and stress-corrosion cracking. Tests of Inconel 132 welds and a bimetal weld-cladding joint between Inconel and Type 308 stainless steel were also made. The test results show that the two heats of Inconel tested possess a rate of metal loss up to 9 mg/dm^2-mo. No stress-corrosion cracking, intergranular corrosion, or selective attack of weld samples or cladding samples was found. Hydrogen-bearing water was the least corrosive and produced virtually no attack. The addition of ammonium hydroxide resulted in a smaller amount of corrosion than that observed with neutral water. Some effects of heat-treatment were evident in tests with ammoniated hydrogen-free water. (auth)—NSA. 19155

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6.3.10, 6.3.3, 3.2.3

On the Mechanism of Oxidation of Nickel and Chromium Base Alloys. (In Russian.) D. V. Ignatov and R. D. Shamgunova. Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk Met. i Toplivo, No. 3, 83-87 (1959) May-June.

The effects of alloying elements (aluminum and titanium) concentration, temperature, and oxidation time on oxidation kinetics, structure, composition and rate of oxide film deposition were investigated. Specimens with 80 percent nickel and 20 percent chromium; nickel with 20 percent chromium and 1, 4.18, 7.22, and 10 percent aluminum; and, chromium-nickel-titanium with 20 percent chromium and 0.68, 3.44, 5.88, and 9.76 percent titanium were tested at 600 to 1000 C.—NSA. 19240

6.3.10, 4.3.2

New Nickel Alloy Cuts Hot Sulfuric Bite. T. E. Johnson. Chem. Eng., **66,** 194, 196, 198 (1959) Dec. 14.

New nickel-chromium-copper-molybdenum alloy, Illium 98, resists corrosion by hot sulfuric acid over a wide range of concentrations. It is readily machinable and weldable but cannot be used with halogen acids.—RML. 19236

6.3.10, 4.3.2

Corrosion Keys—Hastelloy Alloys. J. R. Schley. Haynes Stellite Co. Chem. Processing, **21,** No. 7, 125, 127; **ibid.,** No. 11, 61 (1958) July, Nov.

No. 7: Graphic data on corrosion of hastelloys B, C, D, and F in: Acetic formic, hydrochloric, nitric, phosphoric and sulfuric acids.

No. 11: Graphic data on corrosion resistance of Hastelloys B, C, D, and F, and Haynes Alloy No. 25 and Multimet in hydrofluoric acid, sodium hydroxide and H_2CrO_4.—INCO. 18946

6.3.10, 4.7, 3.7.4

Reflections on the Hot-Zone Attack of Inconel by Fused Fluoride. J. L. Scott. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-58-8-87, August 22, 1958, 18 pp. Available from Office of Technical Services, Washington, D. C.

Evidence is presented that the hot-zone attack of nickel-base alloys in contact with fused fluorides occurs by a grain-boundary diffusion process. Predictions based on the grain-boundary diffusion model are shown to compare favorably with existing data. Certain anomalies are pointed out with regard to the corrosion of Inconel by Fuel No. 30 (sodium fluoride-uranium tetrafluoride-zirconium fluoride) and tests which would lead to a better understanding of fused-salt corrosion are outlined. (auth)—NSA. 18942

6.3.11

The Noble Metals in Research and Industry. H. Wolf. Metall, **12,** No. 7, 585-598 (1958).

A review of recent literature on the mechanical and physical properties of silver, gold and the platinum-group metals (iridium, osmium, palladium, platinum, rhodium and ruthenium), the phase diagrams and structures of their alloys, their chemical, electrochemical, corrosion, and corrosion-protection properties and the industrial applications of both the metals and their alloys. 276 references.—MA. 18982

6.3.15, 3.7.4, 3.7.3

Titanium Alloys Today: How Commercial Alloys Compare. Paul D. Frost. Metal Progress, **75,** No. 4, 91-96 (1959).

Alpha-titanium alloys are strong and have good oxidation-resistance at elevated temperatures. α/β and β alloys are difficult to weld, but their properties may be improved by heat-treatment. The loss of ductility occurring in α/β alloys hot worked in the β-range is related to grain growth of β and is not caused by acicular or grain boundary α.—MA. 19152

6.3.15, 3.8.2, 3.8.3

On the Theory of Titanium Corrosion. W. R. Fischer. Werkstoffe u. Korrosion, **10,** No. 4, 243-250 (1959).

The corrosion behavior of titanium is explained by means of a current/voltage diagram. The region below the minimum corrosion potential is of no practical importance; above this is a hydride-passive region, followed at a critical voltage by chemical activity, corrosion and hydrogen evolution characteristic of behavior in non-oxidizing acids. After a critical potential an oxide film forms and titanium again becomes passive. This is characteristic of the good corrosion-resistance of titanium in oxidizing media. At relatively high potentials, encountered only under anodic polarizing conditions and in the presence of halides, attack again occurs—the transpassive state. Examples are given. 35 references.—MA. 19127

6.3.15, 3.7.2, 4.3.2

Titanium for Process Equipment—New Alloys. Chem. Eng. Progress, **55,** No. 4, 114, 120 (1959) April.

The addition of as little as 0.1 percent palladium to titanium has been found to produce an alloy resistant to boiling solutions of reducing acids without impairing the metals' resistance to oxidizing acids. Mechanical and working properties are unaffected. Equal improvement in corrosion can also be affected by addition of most of the other noble metals. The choice of palladium is dictated by its price, lowest of any of the noble metals.—NSA. 19076

6.3.15, 3.6.8

Cathodic Polarization and Cathodic Corrosion of Titanium in Dilute Sulfuric Acid. (In Japanese with English Condensation.) Rikuro Otsuka. J. Electrochem. Soc., Japan, **26,** No. 10-12, 619-624 (1958) Dec.

Study of electrochemical behavior and

corrosion rates of titanium, polarized cathodically in naturally aerated diluted sulfuric acid, at room temperature. Mechanism of the protective effect of titanium hydride formed on the surface.

Corrosion rate increased with activation caused by cathodic current; corrosion rate decreased with increasing current-density either in a passive or active state. 18910

6.3.15, 3.7.3

Gaseous Corrosion of Titanium-Base Alloys Subjected to Furnace or Induction Heating. (In Russian.) V. A. Yakovlev and Ya. I. Spektor. Metalloved. i Obrabotka Metallov, **1958,** 52-56, June. Translation available from: Henry Brutcher, P. O. Box 157, Altadena, California.

Corrosion in furnaces with moist air is more intensive than in those with air dried by high temperature. Corrosion in undried atmosphere rapidly rises at 700. In induction heating to 1200 at the rate of 10-50 per sec. the depth of change in the surface layer is 5-6 times less than in furnace heating. Scale formation in induction heating is shifted upward about 200 when the rate of heating is increased. 4 references.—MR. 18979

6.3.15, 3.8.2

Electrochemical Investigation of Unalloyed Titanium and of Titanium-30% Molybdenum. O. Rüdiger and W. R. Fischer. Z. Elektrochem., **62,** No. 6/7, 803-810 (1958).

Potential/c.d. curves are used to study the breakdown of deposits formed on titanium and titanium-30 percent molybdenum in various electrolytes. Breakdown potential depends on temperature concentration, and stirring of the electrolyte. Breakdown potentials are given for various halide ions. Figures in mm/year are given for the attack of various strong acids on the very corrosion-resistant titanium-30 percent molybdenum alloy; breakdown of passivity does not occur except in solutions containing hydrofluoric acid; when breakdown occurs the alloy dissolves giving off hydrogen.—MA. 18934

6.3.15

Titanium and Its Uses. (In French.) Usine nouvelle (Numéro Spécial), **1958,** 241, 243-245, 247-249, 251, 253, 255.

A collection of extracts from various sources, British and American. Alloys and their properties, resistance to aggressive chemicals, cladding with titanium, and uses in aircraft are reviewed. —MA. 18994

6.3.20, 3.5.4, 4.6.2, 4.7

The Technology of Zirconium and Its Alloys. Part 2. Corrosion Behavior in Contact with Various Media; Mechanical Properties, Including Tensile and Impact Strength, Creep Properties and Effects of Neutron Irradiation. D. R. Harries. Atomic Energy Research Establishment, Harwell, Berks, England. Chem. & Proc. Eng., **40,** 363-368, 378 (1959) October.

The corrosion behavior of zirconium and its alloys in contact with gasses, high-temperature water, steam and liquid metals is discussed. The mechanical properties, including hardness and tensile and impact strength are reviewed. The results of creep tests on zirconium, Zircaloy-2, and Zircaloy-3 are given. Neutron irradiation effects on zirconium and its alloys are discussed. —NSA. 19204

6.3.20, 4.3.2, 3.8.2

Electrolytic Disintegration of Zircaloy-2 in Nitric Acid Solutions. Walter E. Clark and Sigfred Peterson. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-2824, November 27, 1959, 18 pp. Available from Office of Technical Serivces, Washington, D. C.

Zircaloy-2 is anodically converted to scaly zirconium dioxide at 60 C in 8 M nitric acid. About 0.5 mole of acid is consumed per faraday, and after saturation of the electrolyte with nitrogen oxides about 0.3 mole of gas is evolved per faraday. The nitric acid is reduced to hydrogen, nitric oxide and nitrogen dioxide with hydrogen predominating if the cathode is Zircaloy and nitric oxide if the cathode is platinum. Corrosion specimens of HRT metals were exposed to the electrolysis conditions. From determinations of the decomposition potential of nitric acid it appears that a metal container for the electrolytic process can be protected from stray-current corrosion by holding it at a potential ~ 0.5 volt positive to a platinum cathode operating at a current density of 5 to 10 ma/cm^2. Practical laboratory experiments tended to confirm this conclusion. (auth)—NSA. 19069

6.3.20

Chemical Properties of Zirconium. Alluminio, **28,** No. 3, 125-132 (1959).

Zirconium and its alloys with 1-2 percent hafnium and the Zircaloys (with tin and iron and with or without nickel and chromium) are reviewed. The effects of carbon, oxygen, nitrogen and hydrogen are outlined and the physical and mechanical properties and capture cross-sections to thermal neutrons of zirconium and its common alloying elements are given. Tensile properties and hardness, thermal constant, and the effect of oxygen on electrical conductivity are shown and a table of the resistance to numerous corrosive agents, mostly inorganic but including organic acids and solvents, is appended.—MA. 19015

6.3.20, 3.7.2, 4.6.2

The Effect of Silicon on the Hot Water and Steam Corrosion Rates of Zircaloy-2. M. D. Carver and H. Kato. Bureau of Mines, USBM-U-378, Dec. 10, 1957 (Changed from Official Use Only October 20, 1959), 11 pp. Available from Office of Technical Services, Washington, D. C.

The effects of silicon in the range of 40 to 372 ppm on the resistance of Zircaloy-2 to the corrosive action of pressurized hot water and steam were investigated. The data were inconclusive that the corrosion rate in hot water varied with silicon content. But the data showed the corrosion rate in pressurized steam to increase slightly with increasing silicon content in the range of 149-372 ppm silicon.. (auth)—NSA. 19055

6.3.20, 4.6.1

Hydrogen Pickup During Corrosion of Zirconium Alloys. Warren E. Berry, Dale A. Vaughan and Earl L. White. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-1380, September 24, 1959, 19 pp. Available from Office of Technical Services, Washington, D. C.

Several factors such as alloy composition, hydrogen content of the alloy, surface hydrides and hydrogen content of the water have been investigated for their effect upon the amount of hydrogen picked up by zirconium alloys during corrosion in 680 F water. Metallic additions of nickel increase hydrogen pickup, antimony, chromium and iron appear to decrease the hydrogen pickup, while the addition of tin has little or no effect. The hydrogen content of the metal (50 to 400 ppm) or of the water (0 to 2 atm of hydrogen pressure) does not appreciably change the amount of hydrogen pickup by the alloys studied. It is proposed that certain intermetallic compounds provide cathodic areas which aid in the concentration of hydrogen at the compound. The amount of corrosion-produced hydrogen entering the metal is controlled by the reaction of hydrogen with the particular compound. The hydriding of Zircaloy-2 by gaseous hydrogen is stopped when small quantities of water vapor are added to the hydrogen. (auth)—NSA. 19037

6.3.20, 3.7.3

Relationship of Cooling Rate to the Corrosion Resistance of Zircaloy-2. L. S. Rubenstein, J. G. Goodwin and F. L. Shubert. Westinghouse Electric Corp. Paper from "Bettis Technical Review, No. 10, Reactor Metallurgy." WAPD-BT-10, October 1958, pp. 23-30. Available from U. S. Office of Technical Services, Washington 25, D. C.

A program was conducted to develop a post-fabrication heat treatment which would improve the corrosion resistance of Zircaloy-2 and Zircaloy-3. Samples representing vacuum- and inert-atmosphere-melted materials were tested after receiving a variety of heat treatments. Results indicate that it is advisable to follow any heat treatment in the beta or alpha-plus-beta phase region with a rapid cooling rate of greater than 90 F/min. (auth)—NSA. 18925

6.3.20, 3.7.2, 3.8.4, 3.4.6

On Oxidation-Resistant Phosphor Zirconium Alloy. Rept. I. (In Japanese.) Jin-ichi Takamura and Yasuo Sasaki. J. Japan Inst. Metals (Nippon Kinzoku Gakkaishi), **22,** 663-668 (1958) Dec.

This study was undertaken in an effort to provide a clearer picture of the oxidation mechanism whereby nitrogen reduces the heat resistance of zirconium and also to develop a new heat-resistant zirconium alloy containing a small amount of phosphorus. The oxidation test was carried out in dry oxygen and in air at temperatures of 700 to 900 C using the weight-gain method. Since the oxidation process of zirconium has been explained by the diffusion of negative ion vacancies through the oxide, the factors determining the concentration and the mobility of the vacancies require further examination. They are the valency, the ionic radius, and the ionization potential of the alloying element and the electroneutrality in the oxide lattice. Under such considerations, phosphorus was chosen for the alloying element. The results obtained are as follows: (1) Addition of a small amount of phosphorus counteracts the harmful effect of nitrogen in zirconium and exceedingly prolongs the breakaway period. It is noted that there is an optimum content of phosphorus. The amount ranges from 0.03 to 0.06 wt. percent according to the purity of zirconium. The beneficial effect may be attributed to the solution of phosphorus in zirconium dioxide lattice as P^{5+}, with consequent reduction of the concentra-

tion and the mobility of negative ion vacancies. An excess amount of phosphorus is harmful. (2) The exponent n for the equation of the oxidation process was obtained in pure zirconium and phosphor zirconium alloys. The activation energies of 38,000 and 34,000 cal/mole were determined for pure zirconium in dry oxygen and air, respectively. (auth)—NSA. 18996

6.3.21, 1.6

The Metal Thorium. Harley A. Wilhelm, Editor. Proceedings of the Conference on Thorium Held October 11, 1956 at Cleveland, Ohio. Book, 1958, 402 pp. Available from the American Society for Metals, 7301 Euclid Ave., Cleveland, Ohio.

The following topics were presented at the conference: role of thorium metal in the nuclear field; nonnuclear application of thorium; thorium in magnesium technology; production of thorium compounds; preparation of thorium dioxide and thorium fluoride from thorium nitrate; development of the thorium tetrafluoride-calcium process for thorium metal; preparation of iodide thorium consumable-electrode arc melting of thorium; electrolytic refining of thorium; physical constants, crystal structure, and thermodynamic properties; electronic structure of thorium metal; preferred orientation in thorium; mechanical properties of thorium and high-thorium alloys; recrystallization of thorium; fabrication and cladding of thorium metal; corrosion of thorium and its alloys effects of irradiation on thorium; metallography of thorium; hazards associated with thorium metallurgy; constitution of thorium alloys; chemical analysis of thorium metal; and spectrographic analysis of thorium.—NSA. 18993

6.4 Non-Ferrous Metals and Alloys—Light

6.4.2, 3.8.3

Anodic Behavior of Aluminum at Low Potentials. J. V. Petrocelli. The International Nickel Co., Inc. J. Electrochem Soc., **106,** 566-570 (1959) July.

Electrode potentials, differential capacities, and anodic polarization curves have been determined for aluminum in sulfuric acid solutions. It is shown that the anodic behavior in the region of low potentials (—1.0 v to +3.0 v, S.C.E. scale) follows the relationship $i = \alpha \exp(\beta F)$. Differential capacity measurements show that the capacitance is inversely proportional to the potential. The analysis of the experimental data indicates the existence of a very thin film on the aluminum in this low potential region. It is suggested that the passive behavior of aluminum is due to the presence of a thin, compact, and continuous "oxide like" film on its surface. This film is formed and/or modified by the electrochemical action which takes place between the aluminum and the electrolyte. 18499

6.4.2, 4.6.1, 3.7.4, 3.7.3, 3.2.2

Corrosion Tests by High Temperature Water on Monocrystals of Aluminum of 99.99% Purity. Influence of the Deformation and Restoration After Cold Working. (In French.) P. LeLong and J. Hérenguel. Centre de Recherches d' Antony, Paris. J. Nuclear Materials, **1,** 58-72 (1959) April.

Monocrystalline and Polycrystalline specimens of high-purity aluminum (99.99 percent), prepared from wrought metal, were subjected to corrosion by water at temperatures above 100 C. By micrographic examination, the principal mechanisms of attack were identified and their kinetics studied. It is observed that: (1) a uniform film is first formed over the whole surface and, as previously shown, in the grain boundaries; (2) an irregular type of attack follows, accompanied by pitting; (3) the latter first outlines a network pattern (trace of the dendritic solidification texture) and appears in the grain boundaries, hence the influence of the impurity distribution is revealed even in this high-purity metal. The growth phenomenon previously observed with polycrystalline sheet specimens during corrosion also occurs with monocrystalline specimens. As in the case of the air-oxidation of zirconium, the metal creeps under the influence of the tension produced at the metal-oxide interface. Cold working tends to reduce the corrosion rate and attenuates or prevents a specimen growth; however, it does not appear to diminish the selective attack of the grain boundaries. Heat treatment of the cold-worked specimens at different temperatures produces a progressive change in corrosion behavior, but it is not until the first recrystallized grains appear that the corrosion behavior again approximates that of fully annealed metal. (auth)—NSA. 18423

6.4.2, 3.5.8

Fatigue Damage and Crack Formation in Pure Aluminium. D. R. Harries and G. C. Smith. J. Inst. Metals, **88,** No. 4, 182-185 (1959-1960).

A statistical study was made of the effects of intermediate annealing on fatigue life of aluminum specimens tested in alternating torsion. Annealing at various stages of the fatigue life proves to have no significant effect on the total life to fracture. However, periodic removal of the surface layers during the test enables the fatigue life to be extended considerably. It is concluded that fatigue cracks initiate at the free surface of an even, axially stressed specimen. This is probably due to differences in the modes of deformation of the surface and the interior and not to the corrosive effect of the atmosphere. (auth)—MA. 19201

6.4.2, 4.3.6

Action of Dilute Solutions of Some Inorganic Compounds on Aluminum. L. M. Dye and Charles F. Poe. University of Colorado Studies, No. 2, 65-70 (1959).

Pure sheet aluminum submerged in various salt solutions of different concentration for tabulated times. Loss in weight recorded showed wide range of effect. 9 references.—RML. 19116

6.4.2, 5.9.4

Some New Practical Experience in the Surface Finishing of Aluminium (and Aluminium Alloys). A. Domony, E. Lichtenberger-Bajza and P. Csokán. Metalloberfläche, **13,** No. 3, 84-87 (1959) March.

High-purity aluminum with and without calcium additions up to 0.28 per cent, Anti-corrodal, two aluminum-zinc-magnesium and two aluminum-magnesium silicon alloys, aluminum-magnesium and an aluminum-copper-magnesium alloy were: a) immersed in boiling, distilled and tap water, with and without addition of 2 per cent hydrogen peroxide, 2 per cent sodium hydroxide, or glycerine, or 1 per cent ammonium hydroxide; b) anodized, followed by treatment in hot water with and without addition of water glass. With decreasing purity of the aluminum the barrier-layer thickness, which is very small for 99.99 per cent aluminum, increases, while the total film thickness decreases; the barrier-layer thickness is proportionately very high with all the alloys other than aluminum-magnesium and aluminum-copper-magnesium. Film thickness, brightness and smoothness depend, principally, on the chemical and technical properties of the material; intermetallic compounds and nonmetallic impurities should be absent, while the material must have a good surface finish—in many cases, better results are obtained with a lower-grade metal that has been carefully processed to the semi-finished state, then with a carelessly processed high-purity material. 15 references.—MA. 19095

6.4.2, 3.2.2, 4.6.6, 5.9.4

Pitting of Aluminum in Synthetic Waters. D. E. Davies. J. Applied Chem., **9,** Pt. 12, 651-660 (1959) Dec.

Corrosion characteristics of commercially pure aluminum in synthetic "tap" waters containing sodium chloride, calcium carbonate and dissolved copper. In presence of any 2 of constituents, loss in weight is very small, but nodular pitting is observed when all 3 are present. Maximum weight loss occurs when Ca^{2+} content is 50 ppm, irrespective of chloride ion concentration, copper content being constant. Specimens which have been anodized and subsequently sealed, show no pitting in 2 weeks; unsealed specimens are less effective in this respect. Localized corrosion is most severe after oxide film has been removed in a phosporic/chromic mixture. Mechanism is offered to explain initiation and development of pitting. Effect of anodized film is also considered. Photos, tables, graphs, 15 references.—INCO. 19083

6.4.2, 3.5.9, 8.4.5

Aluminum Alloys for Water-Cooled Reactors. J. B. Cotton. Imperial Chemical Industries, Ltd., Widnes, Lancs, England. Nuclear Power, **4,** No. 42, 100-102 (1959) Oct.

Alloys of aluminum which withstand temperatures at 300 C for long periods of time are reported. These alloys are basically aluminum-iron-nickel with additions of silicon, titanium, beryllium or zirconium.—NSA. 19062

6.4.2

Production, Properties and Possible Applications of Superpurity 99.999 per cent Aluminum. Hans Schmitt and Walter Koch. Z. Erzberg. u. Metallhüttenwesen, **11,** No. 9, 427-430; disc., (E. A. Bloch), 431-432 (1958).

1) Corrosion July—8 OS x 13.5 solid

A new design of three-layer electrolytic cell is described, which operates without any of the disadvantages associated with the conventional cell including the use of graphite cathodes. Feed is aluminum of ≮99.0 per cent purity, producing aluminum of 99.99906-99.99924 per cent purity. Refined photometric methods of determining copper, iron and silicon are described. After remelting, continuous casting and hot and cold rolling, soft annealed strip has 0.2 per cent P. S. and U. T. S. of, respectively, 1.2-1.5 and 4.1-4.5 kg/mm², elongation of 40-50 per cent, and B. H. N. of 15.4 kg/mm²; it is 12 and 24 times more resistant to corrosion by, respectively, 10 and 20 per cent hydro-

chloric acid than is 99.99 per cent aluminum and has enhanced electrical conductivity. Possible applications are in the electrical and radio industries, reflector manufacture and satellite construction. In the discussion, E. A. Bloch comments on the nature and the amounts of the impurities in this superpurity metal in regard to quality definition and standard specification.—MA. 18941

6.4.2, 3.5.7, 4.6.2

An Oxidation Reaction Highly Dependent on Pressure. N. J. M. Wilkins and J. N. Wanklyn. Nature, **182,** No. 4636, 653-654 (1958).

An alloy of aluminum-2.5 wt. per cent nickel was exposed to steam at 325 C and pressures (p) of 550-1500 lb/in.^{2} for times (t) up to 160 hr. The oxidation rate $\propto t^{0.8}p^n$, where $n = 3.9$-4.3. —MA. 18986

6.4.2, 8.10.3

Aluminum Products Finding Big Market in Canadian Mines. B. H. J. Edmond. Precambrian, **31,** No. 12, 12-17, 20, 22 (1958) Dec.

Introduction of aluminum equipment for surface and underground mining operations is one of biggest advances in Canadian mining in recent years. Aluminum alloys offer desirable strength/weight ratio, resist most forms of corrosion, minimize danger of sparking, are non-magnetic, easy to form, have high elasticity permitting rough treatment and shock loading, and have increased their mechanical properties at very low temperatures. Mining applications considered include: cages and skips, mine cars, tubs and trucks, conveyers and loaders, industrial pipe and tube, pulleys, sheaves, idler rolls, mining tools, roof supports, rock bolts, concrete forms, surface buildings, rail cars, boom for conveyers and cranes, dump trucks, and drilling rigs. Fabrication, maintenance and repair are discussed. Corrosion characteristics of aluminum are explained. Table lists mechanical properties of aluminum alloys commonly used in mining industry.—INCO. 19137

6.4.3, 6.6.6, 5.8.2

Beryllium and Its Alloys. Ian S. Plumtree. Machine Shop Mag., **19,** No. 12, 734-737 (1958).

A review of the commoner beryllium alloys and their properties and usages, instancing the corrosion-resistance, non-magnetic and non-sparking qualities of beryllium. The use of beryllium oxide as a refractory material and as a tarnish-inhibitor on silver are mentioned. —MA. 18932

6.4.3

Beryllium: A Search of the Unclassified Literature. Wanda G. Bradshaw. Lockheed Aircraft Corp., November, 1959, 58 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 161012).

Fabrication methods studied included powder-metallurgy methods, extrusion, forging, casting and welding. Methods for cladding beryllium and special techniques for the electrodeposition. Special techniques of purification. Properties of beryllium, such as general metallurgy, physical and mechanical properties, crystallography, effects of radiation and the stress resistance. Corrosion resistance of beryllium under gaseous atmosphere such as oxygen, nitrogen, carbon dioxide and hydrogen. Resistance of beryllium to liquid metals, various aqueous media and organic media. Solid interdiffusion of beryllium with other metals at elevated temperatures. Information available on the alloys of beryllium with aluminum, copper, chromium, iron, magnesium, molybdenum, niobium, nickel, titanium, thorium, uranium, vanadium and zirconium. The toxicology of beryllium, its hazard limits, suitable laboratory and machining methods, and possible means of detection. 241 references.—GRR. 19045

6.4.4, 3.4.9, 5.8.1

Inhibition Between 350 and 500 C of the Corrosion of Magnesium by Humid Air. (In French.) Raymond Darras and Roger Caillat. Compt. rend., **249,** 1517-1519 (1959) Oct. 19.

It is shown that the formation of a fluorided layer on the surface of magnesium raises from 350 to 490 C the temperature at which magnesium resists corrosion in humid atmosphere. The protective coating may be obtained either by the introduction of hydrofluoric acid into the humid air or by fluoridation of the surface by immersion in a bath of demineralized water containing nitric acid and hydrofluoric acid. In both procedures the quantity of fluorine fixed is quite small, being of the order of 0.005 mg/cm^2 after 600 hr. exposure at 450 C to humid air containing the acid. 5 references.—NSA. 19081

6.4.4, 8.4.5

The Corrosion Resistance of Magnesium and Its Alloys in Nuclear Engineering Environments. P. E. Gallant. Corrosion Prevention and Control, **6,** No. 10, 42-45 (1959) Oct.

Magnesium is used as canning material in gas cooled nuclear reactors due to its low neutron absorption coefficients and its combined compatibility towards fuel and coolant at operating temperatures with adequate strength and commercial availability. Discussion of oxidation behavior of magnesium and magnesium alloys covers breakaway corrosion. Development of oxidation-resistant Magnox alloys (alloys of magnesium with aluminum, beryllium and calcium) which can be melted in air without inflaming, molten metal being retained in oxide skin, is discussed. Beryllium is added in form of aluminum-beryllium master alloy. Calcium improves tenacity of oxide film but, because of welding difficulties, it is confined to minute amounts. Metallurgical behavior of these alloys is considered. From gas cooled reactors, unopened cans are deposited in cooling ponds for several months under 15 ft. of water. To prevent pitting corrosion and cracking of oxide film, pH is maintained at 11 and over with caustic soda. Current work and future prospects in magnesium alloy development are reviewed. Table listing alloying temperatures of magnesium with common metals gives 500 C + for nickel. Graph, 27 references.—INCO. 19149

6.4.4.

Corrosion of Magnesium Alloys Containing Iron and Nickel. J. H. Greenblatt. J. Applied Chem., **9,** Pt. 8, 401-405 (1959) August.

Corrosion rates of two magnesium alloys containing 200 ppm of iron and 2 nickel (actual composition 1.75), respectively were measured in sea water when samples of alloys were coupled to steel cathodes of various sizes, inserted in plastic or steel blocks, and compared with those of magnesium alloys corroding alone. Results obtained indicate that decreased corrosion rate observed on coupling to steel cathodes is due to formation of an oxide film over alloy in accordance with mechanism proposed by Tomashov. Critical current density required for film formation appears, from measurements of current density in alloy-steel couples, to be 50 mA/cm^2. Weight loss-time curves are shown. Data tabulated include effect of hydroxyl ion on corrosion rate of magnesium-2 nickel alloys, anode current densities for couples with varying cathode areas, and weight loss values and areas under current-time curves. 8 references.—INCO. 19167

6.6 Non-Metallic Materials

6.6.4, 3.4.6, 8.4.5

A Study of the Reactions of Graphite with Carbon Dioxide with Reference to Gas-Cooled Nuclear Reactors. T. B. Copestake, H. W. Davidson and B. L. Tonge. General Electric Co., Ltd. J. Applied Chem. (London), **9,** 74-84 (1959) Feb.

The reaction of graphite and carbon dioxide is discussed in relation to the performance and safety of gas-cooled graphite-moderated nuclear reactors. Reaction is promoted by reactor radiation but this radiation-induced process is unlikely to be temperature dependent. The limiting temperature for operating the system graphite-carbon dioxide is, therefore, probably set by the thermal reaction. A wide variety of experimental means was used to examine the thermal reaction and it is concluded that gasification of carbon dioxide is unlikely below temperatures of 600°. This conclusion appears valid even if applied to graphite which has undergone heavy neutron damage. Accelerated life tests covering several thousand hours were used to confirm these observations. These same tests show that gasification of graphite occurs at temperatures above 600° but is strongly inhibited by the presence of carbon monoxide. This provides an additional factor of safety from the reactor point of view. The most pessimistic estimate for the rate of gasification of graphite in carbon dioxide by purely thermal means of 500° is calculated to be 0.1 per cent (by weight) in 20 years. The carbon monoxide observed after exposing graphite to carbon dioxide at temperatures below 600° arises from the formation of a stable oxide on the carbon surface. Carbon monoxide can reduce this surface oxide at 500° and the clean surface produced will adsorb carbon monoxide. Carbon monoxide in contact with ingraphitized carbon may decompose and deposit carbon. This deposition reaction is not self-propagating and leads to an inert carbon surface. (auth)—NSA. 19048

6.6.7

Synthetic Rubbers for Corrosion Protection. St. Reiner. Werkstoffe u. Korrosion, **9,** No. 1, 1-4 (1958) Jan.

The properties and applications of the synthetic rubbers are reviewed. Methods for the bonding of vulcanized high polymers to metals are listed, including the brass process in which a layer of 70:30 brass is first electrodeposited on the metal. A table gives the bond strengths at 20 and 120 C for different combinations of bonding methods and synthetic rubbers.—MA. 19026

6.6.11, 5.4.5

Protection Against Water Absorption and Decay of Timber Logs Used for

Booms. P. N. Grover. J. Timber Dryers' & Preservers' Assoc. of India, **4,** No. 3, 11-14 (1958).

Experiments were conducted with deodar (Cedrus deodara) and kail (Pinus excelsa). Methods for the protection of logs in a boom should aim at preventing both decay and absorption of water. Accordingly oil type preservatives, in particular a 50:50 creosote/fuel oil mixture, appear desirable in combination with a bituminous paint applied over treated timber having moderate porosity and adequate shock resistance.—RPI. 19169

7. EQUIPMENT

7.1 Engines, Bearings and Turbines

7.1

Selecting Bearing Metals that will Not Seize. C. L. Goodzeit. Paper before Am. Soc. Mechanical Engrs., Design Eng. Conference, Chicago, April, 1958. Materials in Design Eng., **47,** No. 6, 105-109 (1958) June.

Table and discussion give information needed to select pairs of bearing metals that will not form strong welded junctions during operations. Seizure resistance is given of metals including cobalt, nickel, palladium, platinum, rhodium and titanium. Anti-seizure properties of alloys are discussed.—INCO. 16518

7.1, 6.3.6, 6.2.1, 8.2.2

First Large Steam Turbine for Operation with a Boiling-Water Reactor. C. W. Elston. Paper before Am. Power Conf., Chicago, March 26-28, 1958. Proc. Am. Power Conf., **20,** 248-257 (1958).

Description of design of 192,000 kw, tandem-compound, double-flow steam turbine being built by General Electric for the Dresden Nuclear Power Station. Laboratory tests showed that of all materials tested, which included nickel steels and Ni-Resist, corrosion rate was not importantly increased by high oxygen except for cupro-nickel and BTH bronze. In the high-pressure section, because of larger pressure drops, chromium containing steels, which have higher erosion resistance, were selected for casings, valves and diaphragms. Diaphragms of intermediate pressure section are also of chromium containing steels. Two diaphragms will be cast of Ni-Resist to obtain a comparative evaluation of this material in actual service. Diagrams, tables.—INCO. 18113

7.2 Valves, Pipes and Meters

7.2, 4.3.3, 4.6.5

Evaluation of Check Valve Materials in Uranyl Sulfate and in Distilled Water. R. Blumberg. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-57-12-72, December 17, 1957, 7 pp. Available from Office of Technical Services, Washington, D. C.

Tests were made on a variety of materials in order to improve the durability of valves in the HRT. As a result of these tests and examination of prior experience, the following recommendations were made: Stainless steel type pH 17-4 for check valve seat material in water service; Stellite No. 3 for check valve seats in fuel service; Stellite Star "J" balls used throughout. In addition, stainless type 347, Carpenter "20," aluminum oxide and Kennametal K-501 were tested in fuel and water. (auth)—NSA. 15717

7.2, 6.6.8

Plastic Piping—8 Years Later. W. D. Greathouse and R. L. McGlasson. Oil & Gas J., **55.** No. 32, 106-112 (1957) August 12.

A guide to intelligent use of plastic pipe in oil-field operations. Three types of currently available materials, extruded plastics, glass-reinforced plastics and plastic coatings are discussed. Preferred use for each type is shown based on maintenance cost, property deterioration in service, temperature-strength characteristics and creep characteristics. Tables, graphs.—INCO. 14910

7.4 Heat Exchangers

7.4.1, 3.2.2, 3.5.8, 4.7, 3.7.4

Metallographic Examination of High Velocity Heat Exchanger (SHE No. 1). R. J. Gray. Oak Ridge National Lab. U.S. Atomic Energy Commission Pubn., CF-56-5-148, May 24, 1956 (Declassified October 9, 1959), 14 pp. Available from Office of Technical Services, Washington, D.C.

Judging from the condition of the tube walls, this heat exchanger was close to failure. The depth of intergranular attack on the inner sodium-potassium surface (0.003 in.) and the depth of subsurface voids on the fuel side (0.007 in.) were more than half the wall thickness and these measurements were only from a few scattered specimens and on one plane per specimen. The grain size was much larger in the hot end than in the cold end of the heat exchanger. This increased grain size in the hot end could be attributed to the absence of precipitate and greater triaxial stresses due to thermal expansion and a thermal differential across the tube wall. Also, the strain anneal effect due to the thermal cycling during operation at a specific temperature would accelerate grain growth. These stress conditions and the resulting change in microstructures are directly related to the operating temperature at the hot end. The greater depth of corrosion at the hot end could also be due to a greater stressed condition or a corrosion fatigue. Mass transfer was present where the sodium-potassium entered the heat exchanger, but this deposition was influenced greatly by flow against the tube walls. The maximum deposit was 0.003 in. (auth.)—NSA. 19171

7.4.2, 6.4.2, 3.4.8

Corrosion Phenomena in Electrolytic Condensers and Their Causes. (In German.) G. Hahn. Werkstoffe u. Korrosion, **11,** No. 1, 28-33 (1960) Jan.

A breakdown and failure of an electrolytic condenser with aluminum electrodes is mainly attributable to corrosion phenomena. These are initiated by the presence of certain cations and anions which may already be present in the raw materials, or may have entered the condenser during the manufacturing process. Compared with aluminum corrosion under normal conditions, the corrosion effect is increased by the prevailing potentials. Moreover, the formation of the 'filter layer' formed by the dielectric in the electrolytic condenser is liable to be disturbed by the slightest impurities in the electrolyte. These phenomena can be avoided by using tantalum anodes and a solid electrolyte. 19205

7.4.1, 8.4.5, 6.2.3

Chemical Experience with the Recirculation Cooling System of the NRX Thermal Shields. G. M. Allison. Atomic Energy of Canada, Ltd., CRDC-854, March, 1959, 18 pp. Available from Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

Mild steel thermal shields in the NRX reactor were cooled for the first eight years by Ottawa River water with added phosphate, alkali and chlorine, on a once-through basis. In the summer of 1955 the cooling system was changed to recirculation, and this report deals with chemical and corrosion results obtained since that time. Considerable difficulty was experienced in raising the pH of the recirculating water to > 9 and keeping it there. This was attributed in part to conversion of the old iron-phosphate corrosion film to an oxide film. The thermal shields have been cooled with recirculating steam condensate at pH 9.0-9.5 for the past three years. Since recirculation began, the rate of increase of iron concentration in the water has dropped from about 6 ppm/day to 1 ppm/day. It was observed that the rate of iron accumulation in the water was affected by reactor operation, being much lower when the reactor was down. The use of ion-exchange resins for purification was restricted to the first few months of recirculation since the columns were far too small to handle the impurities building up in the water. A feed-and-bleed operation involving steam condensate made alkaline with potassium hydroxide was used for a considerable time to control the iron concentration in the recirculating water. Since November, 1957, no purification has been employed. Mild steel corrosion specimens have indicated a corrosion rate of 50-100 mg/dm²/mo in the parts of the system with high flow rates. An iron-release rate of 10 mg/dm²/mo has been calculated from the average iron buiildup in the water of 1 ppm/day. Since the feed-and-bleed procedure was stopped the water has remained essentially oxygen-free, and the hydrogen concentration has been approximately 20 cm³/kg. (auth)—NSA. 18351

8. INDUSTRIES

8.4 Group 4

8.4.5, 3.5.4

Nuclear Problems and Structural Questions in the Construction of Reactors. (In German.) P. Eversheim. Atompraxis, **5,** 362-367 (1959).

The most important physical and thermal properties of the various structural elements of a reactor, which are exposed to nuclear radiation, are described, and the conditions for canning materials, properties of corrosion and the effect of radiation on structural materials are discussed. Metallurgical problems are discussed in addition. (auth)—NSA. 19133

8.4.5, 6.4.2, 6.4.4

An Example of Metallurgical Adaptation of Classical Metals to an Essential Problem in the Nuclear Industry: Aluminum and Magnesium, Canning Materials for Fuel Elements. (In French.) J. Hérenguel. Centre de Recherches d'Antony de la Société des Tréfleries et Laminoirs, Havre, France. Mem. sci. rev. mét., **56,** 273-284 (1959) Aug.

Aluminum and magnesium are of in-

terest to the nuclear industry for fuel element cladding because of their low neutron cross section. For application in this field, the creep resistance must be improved, the deformation capacity after prolonged service must be stabilized, and the corrosion resistance to water at high temperatures must be increased. The results obtained up to the present in the study of these characteristics are reviewed. Some general metallurgical mechanisms are deduced. 36 references.—NSA. 19199

8.4.5

Survey of the Physics, Metallurgy and Engineering Aspects of Reactor Control Materials. General Electric Co. U.S. Atomic Energy Commission Pubn., GEAP-3183, June 12, 1959, 396 pp. Available from Office of Technical Services, Washington, D. C.

A survey of the present state of knowledge of the theory of control in nuclear reactors and a list of references to the literature in this field are presented. Recommendations for a program of work, both theoretical and experimental, are included. The choice of high neutron absorber material for a specific reactor application depends on many factors among which are: nuclear considerations, metallurgical fabricability, radiation stability, corrosion resistance, mechanical strength cost and availability. Materials are discussed from the engineering application standpoint.—NSA. 19153

8.4.3, 4.3.2, 6.2.5, 3.5.9

High-Temperature Hydrogen Sulphide Corrosion in Refinery Experience. P. W. Sherwood. Corrosion Technology, **5**, No. 10, 326-329 (1958) Oct.

Catalytic cracking and desulphurization lead to attack by hydrogen sulfide at high temperatures. Resulting corrosion products hinder heat transfer as well as oil flow. Corrosion begins at a threshold concentration of 0.006-0.008 mole per cent of hydrogen sulfide. Increasing temperature increases corrosion, but increasing hydrogen sulfide concentration has little influence. Protection against hydrogen sulfide attack may be provided by use of chromium-nickel steels or aluminum coating, and by adequate desulphurization of feedstock and recycle gas. Except at very high temperatures (above 1,100 F) good resistance is shown by high chromium-nickel alloy. These alloys are more effective than high-chromium or high-nickel steels alone. For best corrosion resistance, chromium:nickel ratio should be at least 0.5. Table gives corrosion rates for 0-9 chromium, 12-16 chromium and chromium-nickel steel coupons located at strategic points in thermofor catalytic reforming units.—INCO. 18953

8.4.5, 6.4.2

Interim Report on Tests Performed at the K Reactors to Effectively Decontaminate The Process Piping by an Internal Chemical Flush. H. F. Jensen. General Electric Co., Hanford Atomic Products Operation. U.S. Atomic Energy Commission Pubn., HW-56001, May 22, 1958, 13 pp. Available from Office of Technical Services, Washington, D.C.

The chemical flush resulted in corrosion of the aluminum at the rate of 0.04 mils in five minutes using a Turco 4360-B concentration of 3 ounces per gallon at 50 C. Tests indicate that laboratory procedures are inadequate for heavy contamination found in process tubes, however, increasing the Turco concentration and contact time appear to provide satisfactory results. Further tests aimed at optimizing tube decontamination are scheduled. Experimental results are presented graphically and tabularly.—NSA. 19243

8.4.5, 2.3.9, 3.4.3, 3.5.2

Radiochemical Measurements of In-Pile Loop Corrosion Product Deposits and Their Interpretation, July 17, 1955-April 7, 1958. S. Yerazunis and R. E. Larson. Knolls Atomic Power Lab. U.S. Atomic Energy Commission Pubn., KAPL-M-SMS-97, December 31, 1958, 40 pp. Available from Office of Technical Services. U.S. Dept. of Commerce, Washington 25, D.C.

Radiochemical measurements on fuel element cruds, out-of-flux deposits, ion exchange accumulations, and particulate corrosion products circulating in the coolant which were obtained from the KAPL-37 and KAPL-30 test facilities were studied. On the basis of these data, it was concluded that no single transport mechanism could account for the observed effects. A simplified mathematical model describing loop activation by the transport of particulate crud and by the diffusion of active nuclides was derived and applied to the KAPL-37 data. Within the limitations imposed by the assumptions required to develop the loop activation equations and the limits of accuracy applied to the experimental data, the activation of the KAPL-37 loop and fuel element deposits could be described on the basis that 81 to 92 per cent of the influx deposits were transient, and therefore erodable, and that up to 24 per cent of the system crud could take part in an exchange process with the coolant. Resuspension of out-of-flux cruds, a mechanism not included in the loop activation equations, was determined to be occurring in the KAPL-30 facility. Circulating coolant activity as derived from hot crud filter and filtrate samples was found to be considerably less satisfactory than estimates obtained from ion exchange accumulations. (auth)—NSA. 18995

8.4.5.

Tabular Summary of In-Pile Rocking Autoclave Solution Corrosion Data. R. J. Davis. Oak Ridge National Lab. U.S. Atomic Energy Commission Pubn., CF-59-9-75, September 24, 1959, 19 pp. Available from Office of Technical Services, Washington, D. C.

A non-critical tabulation of in-pile rocking autoclave data is presented. Exposure conditions, corrosion data, analytical results and references to other reports are given. Other data on rocking autoclave experiments can be found in ORNL report CF-58-6-92, June 18, 1958. (auth.)—NSA. 19096

Some Metallurgical Features of Nuclear Reactors. H. M. Finniston. J. Joint Panel Nuclear Marine Propulsion, **3**, 17-33 (1959) Oct.

Metallurgical features of fuels, canning materials, and pressure vessels of possible nuclear reactors for ship propulsion are examined. The growth and swelling of uranium and its alloys upon irradiation are considered. Fabrication and corrosion behavior of these alloys are discussed. The properties of aluminum, beryllium, magnesium, zirconium and stainless steels for use as canning materials are discussed.—NSA. 19128

J. M. PEARSON

Contributions of J. M. Pearson to Mitigation of Underground Corrosion

Six articles by the late Dr. J. M. Pearson and one by an associate prepared under his leadership are reprinted for the information of new workers and established investigators into underground corrosion problems. Dr. Pearson, recipient of the 1948 NACE Speller Award for achievements in corrosion engineering, is recognized for his outstanding work on problems associated with corrosion of metals underground. The articles, originally published during 1941-44 in The Petroleum Engineer and in Transactions of The Electrochemical Society are reprinted by permission in this book dedicated to him.

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(c) To encourage special study and research to determine the fundamental causes of corrosion, and to develop new or improved techniques for its prevention.

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Topic of the Month

Underground Aluminum Pipe Line For a Sour Gas Gathering System*

By R. W. FLOURNOY*

Abstract

Bare 6063-T5 aluminum pipe used in a sour gas gathering system was inspected after service in a soil composed largely of sandy loam and broken caliche. Cathodic protection was not applied. Only at points where the aluminum pipe joined a steel line was the former coated and wrapped. Six years service was obtained under these conditions before failure occurred. It was believed that chlorides in the soil caused the pitting which resulted in the failure.

It was concluded that aluminum pipe can be safely installed in neutral soils, sandy dry soils, and dry rock areas. The pipe may be installed bare in underground service if protection by zinc or magnesium anodes is provided for any local "hot spots" which develop. Aluminum appears to have good resistance to the hydrogen sulfide in sour gas. 8.9.3

Introduction

THE GOLDSMITH Gathering System for sour gas was installed in eight different locations late in 1952. Aluminum pipe was selected for this application because of its resistance to hydrogen sulfide and because it could be installed bare without cathodic protection.

Approximately 10,500 feet of 4-inch IPS extruded aluminum alloy 6063-T5 were installed in a soil composed largely of sandy loam and broken caliche. This pipe was 4.5 inches outside diameter with a 0.125-inch wall thickness. The pipe was butt welded using tungsten electrode argon gas shielded electric arc welding process with 4043 aluminum alloy filler wire. The pipe was welded manually using two specially designed dollies for "roll welding" and an internal "back up" and "line up" tool which was removed after each joint was welded. Seven to ten joints were welded per hour using this procedure. At points where the aluminum pipe joined a steel line, the aluminum line was coated with pipe line dope and wrapped for a distance of 40 feet adjacent to the bimetallic junction. The time for welding aluminum pipe was about equal to that for steel pipe of equal wall thickness.

The aluminum line was inspected at several locations after 27 months of service. One inspection was made when a section of the line was damaged during the laying of steel pipes at a point where the ditch crossed the aluminum line. The pipe at this location had a two-foot cover of sandy loam, a loose sedimentary type of soil in a location which could be termed a "hot spot." The exterior of the pipe was free of scale and did not show any pitting. The interior of the pipe, exposed to the sour gas, was also uncorroded and free of pits.

Approximately forty feet of the line was exposed at a second location where the aluminum line connected to a steel line. No insulated bolts, insulating sleeves or insulating washers were used at this bimetallic connection. Inspection indicated that the aluminum was not corroded on the flanges around bolts or in the crevices in bolt holes. Apparently there was insufficient moisture or electrolyte in the soil to cause galvanic attack at the junction of the aluminum and steel lines.

First Failure

The first failure in this aluminum pipe line took place in January 1959. This represents six years of service for bare aluminum pipe before any corrosion was evident or a failure encountered. Examination of the corroded pipe indicated that the failure was caused by pitting from the external side, apparently on the bottom side of the pipe. The pitting indicated that chlorides in the soil could have been a contributing factor in the corrosion.

A qualitative analysis of corrosion products removed from the external surface of the corroded area showed the presence of chlorides. An X-ray diffraction analysis identified aluminum only, while X-ray fluorescence scan showed

Figure 1—General view of aluminum pipe laying operation. Left to right: stock of aluminum pipe, first set of dollies for supporting pipe at welding station, welding machine, welding station, second set of dollies, and truck dragging section forward along ditch.

★ Submitted for publication May 24, 1960.

* Chief Chemical Engineer, Engineering Services Dept., Reynolds Metals Co., Richmond, Virginia.

calcium and a trace of iron. Exact location and soil conditions at the point of failure were not specified. Factors which can contribute to the failure of aluminum pipe lines are (1) soils of high alkalinity, (2) presence of excessive chlorides in the soil, and (3) proximity of the aluminum line to cathodically protected steel lines. No corrosion attack was observed on the internal surface of the aluminum pipe line.

The installation of an aluminum pipe line without protective coatings and cathodic protection is competitive with steel pipe which requires protection. In neutral soils, sandy dry soils, dry rocky areas and certain other soil conditions, aluminum pipe can be installed without external protection. The following procedure is recommended for such proposed installations:

1. Determine soil conditions, specific electrical resistance, pH, chlorides.

2. Install aluminum pipe bare with wire connections attached for pipe to soil measurements.

3. After one to six months' buried service, make pipe to soil potential measurements.

4. Use zinc or magnesium anodes to protect any "hot spots" indicated by pipe to soil potentials.

Conclusions which may be reached from the service obtained by this line are:

1. Aluminum is resistant to the hydrogen sulfide in sour gas.

2. Aluminum pipe may be installed bare in underground service if protection is provided for any local "hot spots" which develop.

Any discussion of this article not published above will appear in December, 1960 issue.

Qualitative Mechanism of Stress Corrosion Cracking Of Austenitic Stainless Steels*

By D. VAN ROOYEN

Abstract

Test results support the electrochemical mechanism of stress corrosion crack initiation in austenitic stainless steel. After a period of initiation, during which partial passivation occurred, local anodes corroded along certain narrow planes, resulting in cracking and ultimate failure. Crack lengths gradually increased with time, after the onset of stress corrosion crack propagation, and no cracking took place during the initiation stage.

Unlike a brittle fracture, which propagates very rapidly, the cracks extended slowly and gradually through austenitic stainless steels and a magnesium-base alloy, without any steps of instantaneous advance. Crack propagation in mild steel, placed in hot nitrate solutions, took place in alternating steps of rapid and slow penetration. The rapid steps were not instantaneous. The stress corrosion cracking of aluminum-4 percent copper and aluminum-7 percent magnesium alloys, in sodium chloride-sodium bicarbonate solutions, consisted of alternating stages of electrochemical corrosion and sudden physical failure.

Study methods used include the automatic recording of electrochemical potential change and extension of specimens, and the acoustic recording of sound generated during cracking. 3.5.8

Introduction

STRESS CORROSION cracking of metals has been a subject of study for many years. Many varieties of alloys are susceptible to this kind of attack. As a result, several different theories have been advanced to explain how cracks form and penetrate into a stressed metal when placed in a corrosive medium. The corrosive action resulting from exposure of the unstressed metal to the same medium is often very mild.

There is little conflict in the concepts about the mechanism of crack initiation, probably because little experimental evidence exists to support any suggested mechanism. It has been difficult to obtain any direct evidence on this point. A sufficiently sharp pit, for instance, formed during the initial stages of attack, becomes part of the subsequent crack, and thus the evidence of pitting is destroyed.

The fact that a fissure is three-dimensional causes another complication. Only one plane is seen in metallographic work, and it is often difficult to determine whether an observed crack started at a certain point on the surface, or whether it spread to that point from somewhere else. It seems to be generally accepted that, in the case of intergranular cracking, localized electrochemical corrosion takes place at susceptible boundaries. The attack, being confined mainly to narrow areas, creates sharp pits. These act as stress-raisers, and consequently cracks are formed and propagation proceeds. A similar sequence of events is believed, by some, to occur in transgranular cracking.

Hoar and Hines hold the view that stress has very little influence on crack initiation in the austenitic stainless steels.[1] They report that the pits formed on this material are usually rounded and unsuitable to act as stress-raisers. In addition, many cracks apparently start in the absence of any pitting. These authors believe, therefore, that crack initation depends entirely upon the exposure of bare metal to the corrosive environment: the greater the area exposed, the greater the chance of exposing a region of suitable susceptibility. The effects of stress level on this mechanism were also reported.[2]

All theories about the mechanism of stress corrosion crack propagation have at least one thing in common: the partial contribution of electrochemical corrosion. Apart from some cases of hydrogen embrittlement, there is apparently no known case of stress corrosion cracking, in an aqueous medium, which cannot be arrested by stopping the corrosion reaction.

The role of stress, on the other hand, is interpreted in many different ways. Hoar and Hines suggested that a crack in stainless steel is propagated by the selective anodic dissolution at its highly stressed advancing edge.[1] Hoar and West elaborated on this idea,[3] and showed that corrosion at very high anodic current densities could occur almost without polarization, if the metal was rapidly yielding, and provided that there was little or no concentration polarization. The above authors are not the only protagonists of the electrochemical mechanism; several others have expresed similar views, but since this does not change the basic argument, these papers are not referred to here.

There has been opposition to the acceptance of the concept that crack propagation occurs entirely as the result of an electrochemical mechanism, mainly because the observed rates of crack propagation seemed to be too high to be accounted for by a corrosion reaction. Consequently, it was suggested that failure resulted mainly from physical fracture.[4,5] In this mechanism, it is postulated that corrosion slowly removes some metal, and then triggers a relatively short fracture. For stainless steel this idea is unproven, but a somewhat similar explanation, with better experimental backing, was advanced to account for the cracking of aluminum alloys.[4,6,7] Thus, intergranular cracking in aluminum-magnesium alloys seems to consist of a series of limited mechanical fractures, which alternate with slow steps in which corrosion plays an important part.

Gilbert and Hadden showed the presence of "negative jumps" in the electrochemical potential during the cracking of this alloy in sodium chlorides,[6] while Edeleanu reported the irregularities existing in the extension of specimens of similar compositions during fracture.[4] Evans and Farmery also concluded that crack propagation took place in steps of physical rupture and electrochemical corrosion along the grain boundaries, and reported similar results for an aluminum-copper alloy.[7] Mears, Brown and Dix discussed earlier the importance of electrochemical corrosion during stress corrosion cracking of other light alloys,[8] without a step-wise mechanism.

Engell and Baumel reported apparent jumps in the potential of mild steel during cracking in nitrate solutions. Their curves, however, were plotted on a compressed time scale, and it was not clear whether or not the changes were instantaneous.[9]

At a recent conference on the stress corrosion of metals,[10] several authors favored the mechanism of alternating steps of brittle fracture and corrosion.[9,11,12,13,14] Nielsen played a recording of what he believed to be the sound of brittle steps during the propagation of cracks in U-bend specimens of austenitic stainless steel.[13] In a subsequent private discussion however, he indicated that he was considering the possibility that the sounds were caused by the formation, evolution or collapse of hydrogen bubbles associated with the corrosion process.

The overall impression gained from a study of the literature is that there is considerable disagreement and uncertainty about the exact way in which cracks penetrate into metals, especially during the stress corrosion cracking of

About the Author

DANIEL VAN ROOYEN is a research engineer in the Metallurgy Department, Westinghouse Research Laboratories, Pittsburgh, Pa. He received a B.Sc. in Chemistry and Physics in 1944 in the Union of South Africa, followed by a Ph.D. (Corrosion) at Cambridge, England, in 1953. He has been studying stress corrosion cracking of austenitic stainless steels since his arrival in this country in 1957.

★ Sumbitted for publication January 28, 1960.

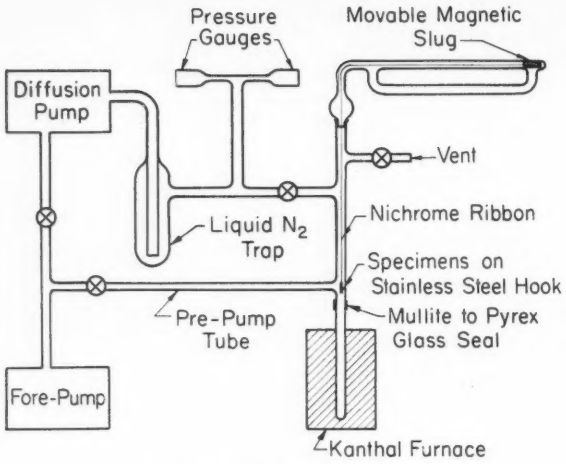

Figure 1—Vacuum annealing furnace.

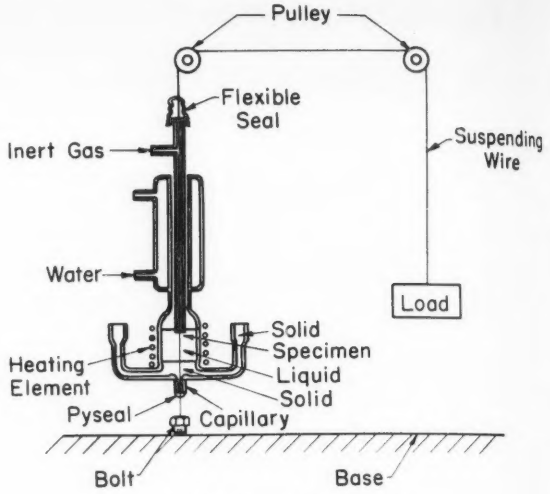

Figure 2—Chemical glass test cell.

stainless steels. It is the author's opinion that a clear understanding of qualitative crack growth is of prime importance, since this would direct the course of further quantitative studies.

This paper gives the results of experiments with several metals used in studies of cracking while observing the electrochemical potential changes, extension in length of specimens during cracking, and the sound, if any, generated in the course of failure. The observations were made in sufficient detail to indicate any sudden steps in the processes, when present. The data obtained led to the conclusion that cracking of austenitic stainless steel in magnesium-base alloy in chloride solutions, is a gradual process without any indication of steps of sudden fracture. Mild steel in nitrate solutions was found to crack in an uneven way, the tests revealing alternating slow and rapid stages. The rapid stages, however, did not approach the speed of brittle fracture.

Aluminum-magnesium and aluminum-copper alloys in a mixture of sodium-chloride and sodium bicarbonate solutions exhibited stress corrosion crack propagation in alternating steps of electrochemical corrosion and instantaneous physical fracture. The purpose of including these light alloys in the present study was twofold: to verify the results in the literature, and to demonstrate the ability of the present methods to detect and record brittle fracture steps, during cracking, if and when they occurred.

As a general conclusion, an electrochemical mechanism of crack propagation is preferred as a major contributing factor in the gradual stages of cracking of any of the materials. There is no evidence, however, excluding the mechanism by which cracks extend under the combined influence of stress and the lowering of surface energy by adsorption on the walls of newly forming cracks.

Experimental

Materials

Stainless steel wires. These test specimens were of 0.023 inch diameter wires of commercial stainless steel having the composition:

Cr	Ni	Mn	Si	C
18.6	9.45	0.71	0.55	0.057

N	Al	P	S	Fe
0.068	0.058	0.035	0.03	Balance

The wires were degreased by washing in acetone and then absolute ethyl alcohol, annealed at 1065 C for 15 minutes in vacuum, at a starting pressure of less than 4×10^{-6} mm mercury, and cooled in vacuum. The cooling was done by rapidly moving the specimens from the hot zone to the cold top part of the furnace, Figure 1; the estimated time taken for the temperature to fall below 400 C was less than 20 seconds. Annealed samples were stored in stoppered tubes until used, and again degreased immediately before each test.

Stainless steel U-bend specimens. Strips of commercial 304 stainless steel, 12x1x⅛ inch, were degreased in acetone. Then they were annealed for 30 minutes at 1065 C in vacuum, water quenched, etched in a 12 percent nitric-2 percent hydrofluoric-1 percent hydrochloric acid mixture at 80 C, rolled to give a reduction of 20 percent in thickness and bent to give an open shaped U. Then the top limbs were pulled into a regular U shape by a bolt passing through the specimen halfway between the top and bottom. The diameter of the bend at the bottom of the U was 1¾ inches. The specimens were never immersed deep enough into the test solution to cover the bolts, so no precautions were taken to prevent metallic contact between specimen and bolt.

Mild steel strips. Strips were cut from 0.05 inch thick sheet of SAE 1015 steel to provide pieces 6 inches long and ¼ inch wide. The specimens were made sensitive to nitrate cracking according to Parkins:[15] they were heated in vacuum at 900-950 C for ½ hour, followed by sub-critical treatment at 690 C for 100 hours. Immediately before testing, the specimens were degreased in acetone and pickled in dilute nitric acid for about ½ minute to decrease the time to failure in nitrate.[9]

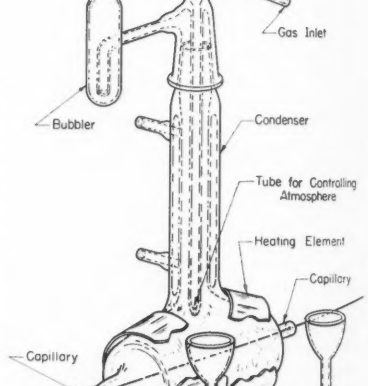

Figure 3—Modified horizontal test cell.

Magnesium base alloy AM-C57S-H. Strips of this material were supplied by ALCOA Research Laboratories in the sensitive state, as described by Mears, Brown, and Dix.[8] A suitable holding piece of the same material was also supplied so that the samples, when placed in the holder, were stressed into the shape of a drawn bow, adjusted to provide sufficient stress to cause cracking in the test solutions in 2 to 3 minutes. The specimen dimensions were 6x13/16x0.064 inches, and they were degreased in acetone just before testing.

Aluminum-copper alloy. Strips of 6x¼x0.05 inches were cut from 96 per-

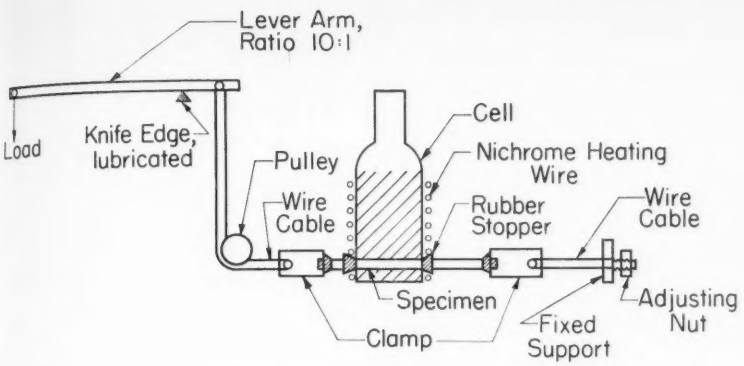

Figure 4—Apparatus with lever system.

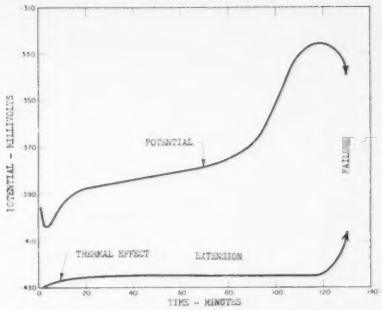

Figure 5—Potential-time and extension-time curves for stainless steel wire specimens.

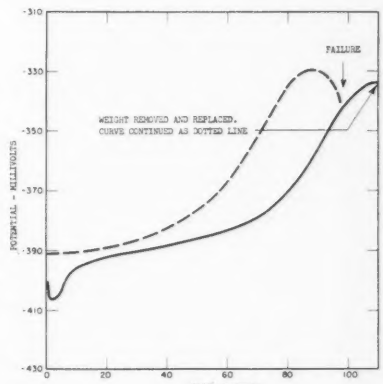

Figure 6—Effect of unloading and reloading on potential of stainless steel.

cent aluminum-4 percent copper sheet, sensitized to cracking according to Farmery and Evans,[7] heated in air at 525 C for 1 to 2 hours, water quenched, and aged at 175 C for 1½ hours. Just before testing, the specimens were pickled in strong sodium hydroxide. The resulting black residual film was left on the specimen during the test.

Aluminum-magnesium alloy. Strips similar to those of the aluminum-copper alloy were made from 93 percent aluminum-7 percent magnesium alloy, solution treated according to Farmery and Evans,[7] and aged at 150 C for 5 days. Immediately before testing, they were treated with aluminum-chloride solution as described in the previous reference.

Stress-Corrosion Testing

All potentials reported were measured against the saturated calomel electrode.

Wire specimens. In many of the initial tests an apparatus very similar to that of Hoar and Hines was used[16] (see Figure 2). The design was changed later so that the specimen passed horizontally through the cell instead of vertically, Figure 3. In both cases the wire was loaded over pulleys by a direct weight. Nitrogen or argon was passed through the small tube leading into the test cell, and in the vertical cell this also protected the water line of the specimen, of which 2½ inches were exposed to the solution. The points at which the specimen passes out of the cell through the capillary are self-sealing, since the concentrated magnesium-chloride solidifies at room temperature. A further refinement to the horizontal cell has recently been made by wrapping the heating element in such a way that heat is only supplied to the bottom half of the cell, thus eliminating the possibility of overheating the upper walls.

The test cell had a capacity of 150 ml, and was preheated for about a minute before the hot solution was poured through the side-arm of the cell. The boiling point of 146 to 148 C was reached shortly after introducing the solution. Before the solution solidified in the colder parts of the test cell, a "liquid" junction was completed between one side-arm and a beaker containing a calomel half-cell in saturated potassium chloride. And when required, a platinum wire was held in a different beaker and connected by a liquid junction to the second side-arm. A current could be impressed between the platinum wire and the specimen.

The potential difference between the reference electrode and the specimen was measured on a "Keithley" 200B electrometer and recorded by means of a "Brush" amplifier and recorder. The recording pen responded to 100 cycles; the chart speed of the recorder could be set at 1, 5 or 25 cm. per second. The sensitivity of the whole assembly was 0.1 millivolt per millimeter; thus, it was possible to detect changes of ¼ millivolt or less.

A clip type strain gauge was incorporated into the apparatus for some of the tests, placed between a fixed point of the stand and the applied load, and connected through a strain analyzer to a "Brush" recorder similar to the one described above. The sensitivity of this assembly was 3.8 millimeters pen deflection per 1 mil extension.

U-bend specimens. U-bend specimens were tested by immersing them to a depth of about 1½ inches into the 42 percent magnesium chloride test solution, which was contained in a glass beaker heated on a hot plate. Liquid junctions for potential measurements were made by means of string bridges and recorded as described before.

Strip specimens. The apparatus used for testing strips of metal is shown in Figure 4. The specimens required relatively large loads, and consequently a lever system was used, lubricated so that it could move freely and without any sound generation. Liquid junctions and potential measurements were made as described before.

The mild steel samples were tested in a solution containing 170 parts $Ca(NO_3)_2 \cdot 4H_2O$, 14 parts H_2O and 3 parts $K_2Cr_2O_7$ by weight. The solution temperature was 110 C, which is about 10 C below the boiling point. The stress level was 32,000 psi.

The two aluminum alloys were reacted at room temperature with 3 percent sodium chloride which was made 0.01N with respect to sodium bicarbonate. The 96 percent aluminum-4 percent copper alloy was stressed at 16,100 psi and the 93 percent aluminum-7 percent magnesium alloy was stressed at 18,600 psi. For both materials other tests were made at somewhat higher stresses, (i.e., just above the yield point.)

Magnesium alloy specimens. These tests were all carried out at room temperature without any externally applied load. The specimen was bent into an arc of a circle, fixed in a holder of similar material, and placed in a beaker of the test solution. Liquid junctions and potential measurements were made as before.

The solutions used were 3.5 percent sodium chloride with 2 percent potassium dichromate in the first case and with 2 percent potassium chromate in the second case. Mears, Brown and Dix[8] reported the first solution to produce intercrystalline failure and the second to produce transgranular cracking.

Acoustic Tests

In addition to measurements of potential changes and the extension of many of the test wires, a system was constructed to detect any sound generated during cracking. This apparatus consisted of a standard record playing arm, the stylus of which could be placed in direct contact with the test piece, lodging in a small indentation previously made by a center punch. The pick-up was connected to a preamplifier to obtain a 100X gain, and this, in turn, could be connected either to a tape recorder for making permanent recordings, or through an amplifier to a loudspeaker for direct listening. The two arrangements were equally sen-

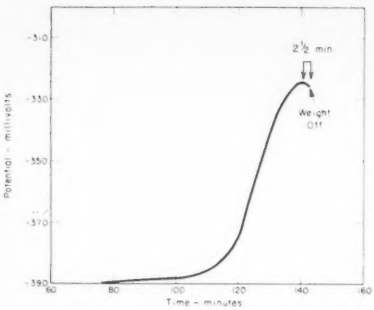

Figure 7—Potential curve showing propagation time before weight taken off and specimen removed (for Type 304 stainless steel wire). Readings extend to 2½ minutes after peak.

Figure 8—The only crack observed in section of specimen treated corresponding to Figure 7.

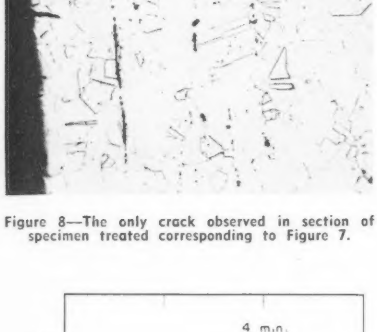

Figure 9—Potential curve showing propagation time before weight taken off and specimen removed (for Type 304 stainless steel wire). Readings extend to 4 minutes after peak.

sitive. The whole assembly acted as a crude type of microphone, and observations made could be recorded during a test by speaking near the apparatus. Before each test the sensitivity of the unit was inspected and set so that a very gentle tap with a hair on the specimen could be heard and, if desired, recorded distinctly. Because of the sensitivity of the apparatus, it was mounted in a vibration-free room, and tests were made under conditions of extreme quiet. In preliminary tests, it was found necessary to exclude devices such as thermostatic

Figure 10—Cracks seen in section of specimen corresponding to treatment as shown in Figure 9.

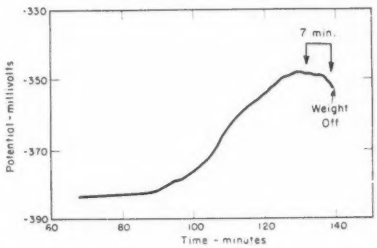

Figure 11—Potential curve showing propagation time before weight taken off and specimen removed (for Type 304 stainless steel wire). Readings extend to 7 minutes after peak.

control units, since they caused very noticeable interference. For tests made in hot solutions the temperature was held constant at 10 C below the boiling point, to exclude noise from steam bubbles.

Results

Stainless Steel

In the work to find the detailed courses of extension and potential changes during crack propagation, it was found that no sudden variations could be demonstrated in any of the samples tested. In addition, it was found that no sound could be heard while cracking progressed through any of the speciments. Extension measurements were made only of the annealed stainless steel wires, and not of any other sample. The general shapes of the potential and extension curves of Hoar and Hines have been confirmed.[1]

Wire specimens. Most of the tests were made at a stress of 40,000 psi. During the first few minutes after the onset of a test, the electrochemical potential of annealed wires fell by about 10 millivolts to reach a minimum of around 410 millivolts negative to a saturated calomel reference cell, recovering again in a few minutes (see Figure 5). During the following period of some 50 to 100 minutes, the potential rose very slowly to the neighborhood of 380 millivolts negative to the calomel reference electrode. A third stage consisted of a rise in potential at the rate of 1 to 4 millivolts per minute, reaching a maximum somewhere between —350 and —300 millivolts. Almost immediately after reaching the peak, the potential began to fall sharply, and this fall continued until the specimen failed by complete fracture. The time taken for the

Figure 12—Cracks seen in section of specimen corresponding to treatment as shown in Figure 11.

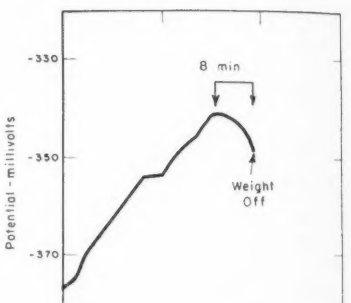

Figure 13—Potential curve showing propagation time before weight taken off and specimen removed (for Type 304 stainless steel wire). Readings extend to 8 minutes after peak.

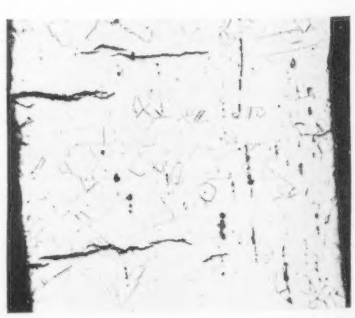

Figure 14—Cracks seen in section of specimen corresponding to treatment as shown in Figure 13.

final stage varied from about 6 to 20 minutes.

In one test a specimen was disturbed by unloading and reloading just after the maximum potential had been reached. The potential returned to that of a freshly exposed wire, and the whole sequence was repeated (see Figure 6). The total time to failure was approximately doubled as a result of the interruption.

In other tests, where the apparatus was only jarred, there were no effects on the potential of time to failure.

Metallographic examination of specimens removed from test after various times of reaction showed no cracks up to the time that the peak in the potential curve was reached. After that time, cracks were seen in the sections. Their

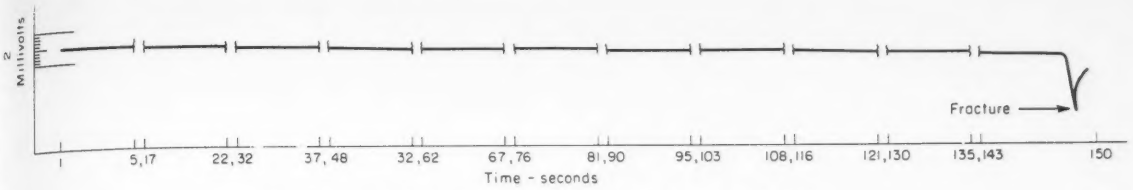

Figure 15—Detailed potential changes during cracking of stainless steel wire.

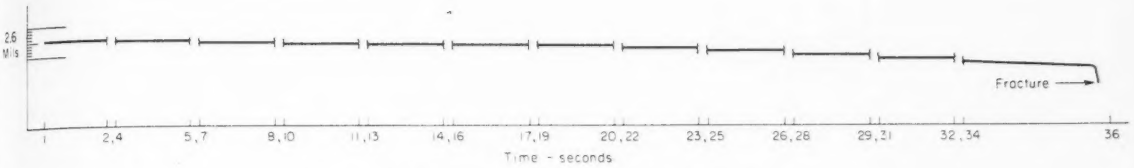

Figure 16—Detailed extension of stainless steel wire during cracking.

lengths increased with the time of reaction allowed after the maximum in potential had been reached (see Figures 7 and 8, 9 and 10, 11 and 12, and 13 and 14). In these figures, as in all others, cracks are approximately normal to the direction of the applied stress.

Extension of the specimens was insignificant during the period corresponding to the rise in the electrochemical potential. At the time when the rapid fall of potential was observed towards the end of a test, a corresponding rapid extension set in, which continued until fracture occurred (see Figure 5).

The detailed courses of both the electrochemical potential change and the extension of specimens during the final period of stress corrosion cracking are shown in Figures 15 and 16. In some cases these curves were not completely straight lines, but at no time, except the final point of rupture, was any instantaneous change recorded.

In the acoustic observations absolute silence prevailed during the whole test, except for a very loud noise at the point of final fracture.

Detailed recordings were also made of the potential changes during cracking of cold-worked wires of Type 304 stainless steel. Some of these wires were swaged to give a reduction in area of about 70 percent when the final diameter of 0.025 in. was reached; others were reduced in area by an estimated 30 percent. Typical potential changes for these specimens are shown in Figure 17. The rise in potential occurred much sooner with these materials. A curve for comparing the response of an annealed sample with the cold-worked materials, at around 130 C, is also given in Figure 17. In all these cases the time of crack propagation is somewhat longer than is usually found at the boiling point. Again, no sudden jumps in potential could be found, the potential fall being gradual during the entire crack propagation period, except at final failure. The acoustic tests again gave negative results; in these tests a 347 stainless steel was included, as-drawn and as-annealed.

It was thought that the cold-worked wires could possibly have a surface much different from that of the annealed materials, which could account for the different potential-time behaviors. Consequently, a sample of each of the three types of wires was well pickled in various mixtures, wiped, carefully washed in distilled water, degreased and tested immediately. Following such treatments a shorter crack initiation time was found for the annealed sample. Furthermore, the pickling shortened the time before the rise in potential even more for the two cold-worked samples. The curve for the untreated annealed sample is given in Figure 17, and the other results are shown in Figure 18. Further work is being done to find the cause of these results.

In general, the effect of the applied load is to decrease the time to failure as the stress is increased. This difference in time to failure, in confirmation of results in the literature,[1] could always be accounted for by a difference in time of crack initiation, while the propagation stage remained the same. There is some variation in the time taken to reach the peak in the curve between various specimens tested under apparently identical conditions. This may possibly be explained when the work described in the previous paragraph is completed.

When a wire specimen was allowed to enter the crack propagation stage (i.e., exceed the onset of rapid potential fall by several minutes), cathodic protection of some 1500 μA/cm^2 prevented the further propagation of cracks already established. Other current densities were not tried since results on this point have become available in the literature.[17]

U-bend specimens. The time to failure of the 0.1 inch thick specimens was approximately 4 hours. Detailed potential changes during this entire period were smooth, resembling the curves obtained from wire specimens as given in Figure 15. The over-all shape of the potential-time curve is given in Figure 19, from which the points of similarity between this and wire specimens can be seen. It was not always easy to tell when the longest crack had gone completely through the material, although some slight pressure with the fingers on the limb of the U-bend sample usually showed whether there was some resistance left; when failure was complete the two limbs of the "U" were loose, although not separated.

Acoustic tests indicated no sound during the entire cracking process, and no sudden rupture occurred even in the later stages of the tests. When a few drops of concentrated hydrochloric acid were added to a test solution in order to try and accelerate the cracking process, gas was evolved from the stainless steel. This gas evolution caused so much noise on the tape recorder, or over the loudspeaker, that the acoustic tests had to be discontinued.

Mild Steel

The overall shape of the potential-time curves agreed reasonably well with those of Engell and Baumel,[9] showing many irregularities. A typical curve is given in Figure 20. There was not always the same number of "jumps" in the curves, and one case, Figure 21, fracture took place without any warning. It was found that the time intervals, during which potential falls occurred, varied from about 15 or 20 seconds up to 2 minutes. Some of these irregularities are shown in Figure 22. The difference between these and the potential drop occurring at the point of sudden rupture of a specimen can be seen by comparison with Figure 23, which is an example of the potential change at failure of stainless steel. Figure 23 can, however, serve as an example, in principle, of the behavior of any metal discussed in this report.

Figure 24 shows the last large fall in potential immediately preceding complete fracture, which took place at point B; from this point there was an instantaneous drop in potential of some 100 millivolts, followed by recovery in much less than one second. Further recovery of the potential to higher values proceeded more slowly. The recovery periods are probably associated with rapid polariza-

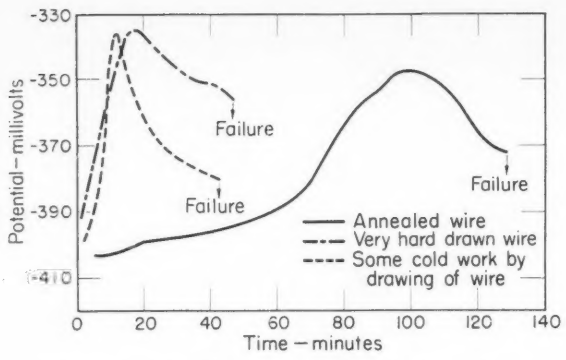

Figure 17—Effect of cold work on potential changes of stainless steel.

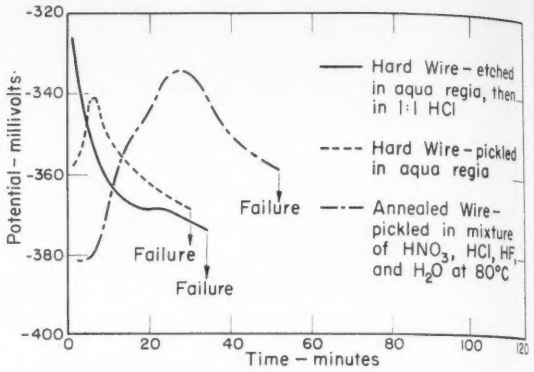

Figure 18—Effect of cold work and etching on potential changes of stainless steel.

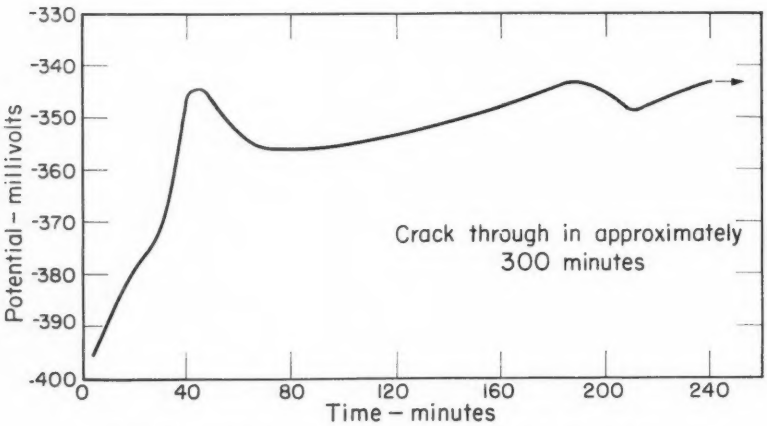

Figure 19—Potential change with time of U-bend specimen of stainless steel.

tion at the freshly exposed metal surfaces.

No sound was associated with the discontinuities in the potential-time curves in any of the tests. In one case some distinct "pips" were recorded, but they were traced to slight boiling due to the fact that the temperature had risen unexpectedly to the boiling point, and bubbles could be observed coming from the test piece. When the test was repeated several times at lower temperatures, no noise could be demonstrated. Final failure, as could be expected, caused considerable noise over the acoustic system in all the tests.

Aluminum Alloys

A typical curve for over-all potential changes with time is given in Figure 25. Results for the 4 percent copper alloy did not differ significantly from this with respect to the irregularities observed. The "jumps," of which there were usually as many as shown in Figure 25, ranged in magnitude from a few to several tens of millivolts in a negative direction. In some tests, especially at higher stresses, fewer steps were found, and two or three samples of the copper-containing alloy broke without any warning. It was found that the addition of a little hydrochloric acid to the test solution not only decreased the time to failure, but greatly increased the number of steps. Towards the end of each of these tests, several "jumps" of a few millivolts each were recorded per second.

In all cases, in the acoustic tests, noise was heard corresponding in time to each potential jump, and no sound was heard without the sudden potential drop. Detailed examination of the course of the potential-time curve indicated that a jump consisted of an instantaneous potential fall followed by a slightly slower recovery. The shapes of these steps are very much like that given in Figure 23.

This series of tests illustrated the capability of the acoustic system to reproduce the sound generated during sudden steps in the course of stress corrosion cracking. In fact, most of these noises were loud, so that much smaller crack steps should be capable of detection.

Magnesium Alloy AM-57S-H

In solutions containing chloride and chromate the potential changed constantly in the active direction until the piece broke; in the solutions with chloride and dichromate the potential became more noble during most of the test, with the curve flattening some seconds before fracture, but in no case did the potential fall except at failure of the sample. The curves are given in Figure 26.

The detailed measurement of potential changes showed a complete absence of steps except at final rupture. Acoustic tests gave completely negative results, again with the exception of considerable sound generation at total failure. Metallographic examination of the broken pieces showed that many cracks had penetrated ¼ to ⅓ of the thickness of the metal before failure at the weakest point occurred.

Discussion

The results confirm and extend ideas regarding the gradual growth of stress corrosion cracks in most of the alloys examined, and especially that of austenitic stainless steel in boiling magnesium chloride. Although this paper is concerned primarily with the nature of crack propagation, a few remarks are included here on the period of crack initiation on stainless steel.

Initiation

When the boiling magnesium chloride solution comes in contact with a stainless steel specimen, corrosion sets in at points of imperfections and gives rise to an initial drop in the electrochemical potential. Many of these exposed areas may become covered by the formation of solid corrosion products, as suggested by Hoar and Hines.[1] As this process continues, the cathodic areas on the surface expand at the expense of anodic areas. This is accompanied by a rise in the potential. As a result of this process, the anodic current density rises, and is sustained at local areas. There the combined effect of the local acidity inside pores, caused by corrosion, and the metallurgical results of applied tensile stress create suitable conditions. Very drastic handling of a specimen at the stage when crack propagation is about to start can disturb the large cathodic area, Figure 6, cause a lowering in the anodic current density, and make a second initiation period necessary before cracking sets in.

The role of stress during the initiation period seems to be negligible and the time to fracture was not affected by the application of the load some time after starting the test. The shape of the potential-time curve for Type 304 stain-

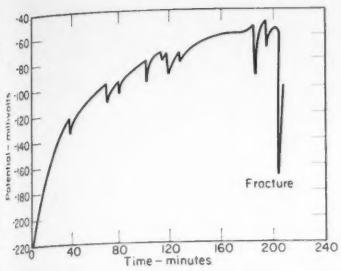

Figure 20—Apparent jumps in potential of cracking mild steel.

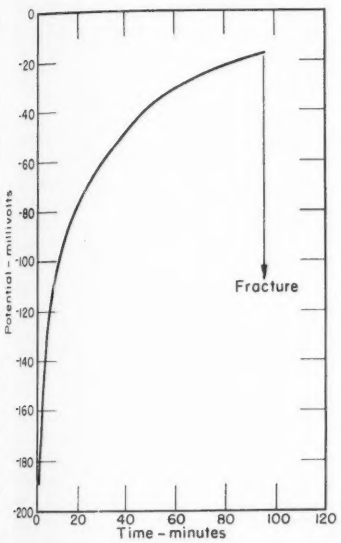

Figure 21—Failure of mild steel without jumps in potential.

less steel, for instance, remains the same during the initial period regardless of the stress level. At low levels, however the time interval between reaching the peak in potential and the onset of cracking is prolonged.

It has been suggested that the number of sites suitable for attack and cracking decreases with applied stress, and that the longer period between partial passivation and failure is caused by the fact that the fewer the susceptible sites, the more bare metal will have to be exposed to the electrolyte before cracking can set in. Since the exposure of bare metal is dependent on film undermining during slow corrosion, fracture at low stresses will take longer than at high stresses.

Support for this argument was given by the experiment of Hoar and Hines which showed the absence of an induction period when some acid was added to the magnesium chloride test solution. In some of the present tests, however, the air-formed film was removed by picking just before the experiment. In these cases the induction period, accompanied by a rise in potential, was of much shorter duration than in the case of the unpickled wires. Since the rise in potential probably indicates passivation by film formation, it seems that while the partial destruction of the original film

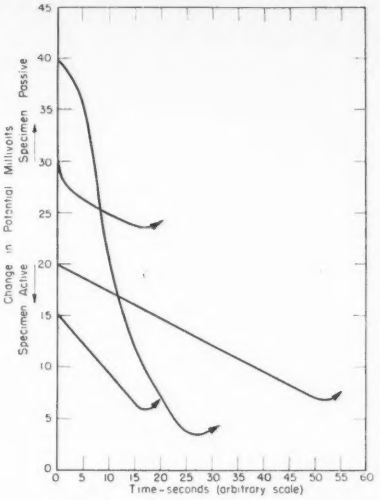

Figure 22—Detailed potential changes of cracking mild steel.

before test exposes more bare metal to the solution, the over-all corrosion rate is too slow to provide cracking in non-acidified magnesium chloride. In these solutions, apparently, at least some film repair is necessary to give sufficiently high anodic current densities which are required for crack propagation. In the case of an acidified solution, higher over-all corrosion rates probably account for the earlier onset of cracking. It is not clear, however, why passivation occurs so rapidly in the case of pickled specimens, and also cold-worked samples. The mechanism may consist of the removal of the existing air-formed film and replacement by a different one, but this point needs to be investigated further before a better understanding can be reached.

Propagation.

The present results indicate that the alloys tested can be divided into three groups according to their mode of cracking:

a. The gradual growth of cracks throughout the propagation period, without any detectable jumps in extension or electrochemical potential change, and with no acoustic indication of instantaneous fracture. In this group are classified stainless steel, with or without prior cold work, and the magnesium-base alloy.

b. The growth of cracks in mild steel in alternating slow and relatively rapid steps, but without any symptoms of sudden physical fracture. During this type of crack propagation, rapid falls in the electrochemical potential occur at various times. All changes require at least several seconds and sometimes one or two minutes, but they are never accompanied by sound generation.

c. Cracking in steps of instantaneous mechanical fracture alternating with a slow stage. This qualitative mechanism is typical of cracking of the two aluminum-base alloys, and is accompanied by sudden negative jumps in electrochemical potential and by cracking noises over the acoustic system.

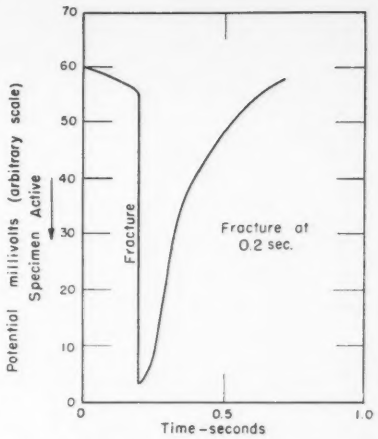

Figure 23—Potential drop at final sudden rupture of stainless steel wire.

Stainless steel. Experimental support for the gradual growth of cracks in this alloy is given in Figures 7 to 16, in which are shown the curves for extension and potential changes, as well as actual crack lengths. These observations agree with those of Hoar and Hines,[3] and confirm the rate of crack propagation as of the order of 1 mm per hour. For similar cracking rates, Hoar and West[3] calculated that an anodic current density of about 0.5 to 2 amps/sq. cm. could account for completely electrochemical crack propagation. There was, of course, the difficulty of polarization which could normally be expected to be considerable under existing conditions. This objection was also discussed by Hoar and West, who demonstrated that stainless steel was capable of corrosion at high current densities with practically no polarization, provided that (1) the material was yielding rapidly under tension, and (2) there was no concentration polarization. Such a mechanism would be consistent with the present results, although it is difficult to see how concentration polarization is avoided.

An alternative mechanism of cracking of stainless steel has been postulated, mainly on the claim that corrosion alone could not account for any reasonable rate of cracking. This mechanism involves alternating steps of slow corrosion and rapid mechanical fracture for a limited distance only.

The same mechanism has also been proposed for several other alloys as discussed earlier. Such a theory would explain an apparently gradual penetration of metals, and would still account for the fact that, in most cases, cracking can be halted by stopping the corrosion reaction, for instance, by applying cathodic protection. It is difficult, however, to see why very high anodic current densities are required for cracking if this mechanism is correct. Thus, as shown in Figure 6, the destruction of highly localized anodic areas, and the provision of a more general corrosion area should not have led to an extended time to failure by the above mechanism. Furthermore, since a stepwise failure would be accompanied

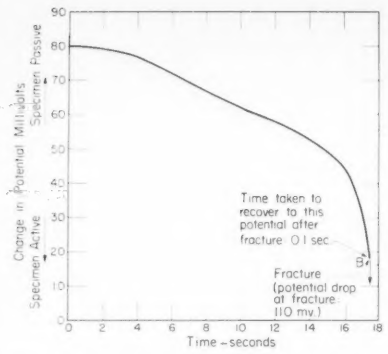

Figure 24—Potential change up to time of complete cracking of mild steel.

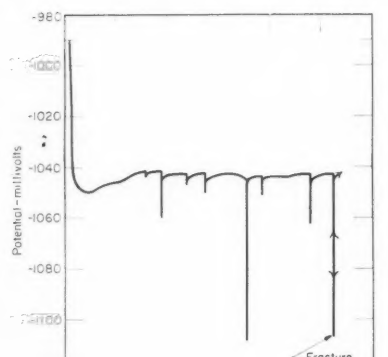

Figure 25—Negative potential jumps during cracking of aluminum-7 percent magnesium alloy.

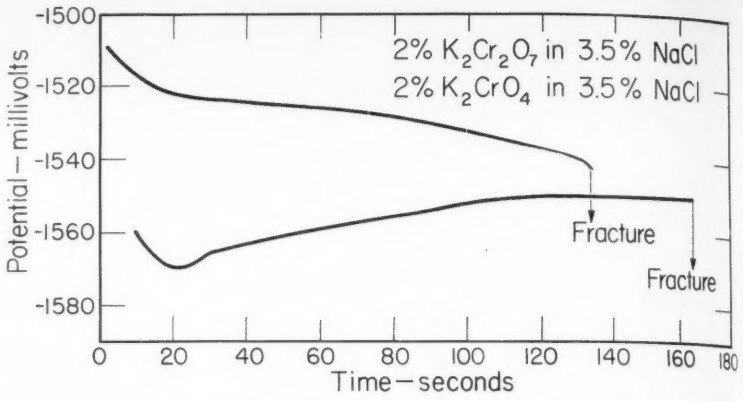

Figure 26—Potential changes during cracking of magnesium-base alloy.

by periods of very rapid surface formation during proposed "jumps," it could be expected that corresponding irregularities would be found in the potential-time and extension-time curves. For stainless steel, however, these curves are smooth. Also, sudden steps of physical failure generate a cracking sound, which can be heard after suitable amplification (as shown in the case of the aluminum-base alloys), but such sounds were never heard during the cracking of stainless steel. Therefore, if any mechanical steps are present in the mechanism, they must be very small indeed in order to escape detection. Any contribution by instantaneous mechanical fracture to the mechanism of stress corrosion cracking in stainless steel is consequently thought to be either insignificant, or in the form of extremely short ruptures. The accent seems more correctly to be placed on the importance of electromechanical corrosion, acting along very narrow planes at high current densities.

Data to exclude other thories based on an electrochemical mechanism have not been obtained, but the mechanism advocated by Hoar, et al., seems to be most acceptable. A possibility exists, of course, that the walls of a crack may act as a suitable cathodic area for the corrosion reaction, thus reducing the apparently high resistance of a long narrow crack.

Polarization as a result of concentration of dissolved metal ions may be low if sufficient diffusion of these species outwards into the wider regions of a crack takes place, where they would be diluted by incoming electrolyte. Another uncertain factor relating to concentration polarization is the configuration of a crack. Apart from the work of Nielsen,[13] and similar suggestions about crack widths by Gulbransen and Copan,[18] very little is known about the exact metal area which is reacting. Such information is obviously very important in calculating the metal ion concentration inside the crack. In view of the difficulty of explaining the absence of concentration polarization inside an advancing crack, therefore, it remains doubtful whether the dissolution of a thin layer of metal is the sole operative mechanism. An alternative explanation for the experimental results could be the lowering of surface energy, by adsorption, to such an extent that spontaneous parting of the metal under tensile stress would take place.[19, 20] A feature of any such mechanism, however, must be that it is under control of a step sufficiently slow to prevent sudden fracture. It is also necessary that the alternative mechanism must explain the absence of cracking in the absence of corrosion.

It is concluded that no single mechanism has been shown to account in full for the phenomenon of stress corrosion cracking in stainless steel, and that it is not unlikely that the cause of cracking is a collective effect with more than one contributing factor.

Where reference to an electrochemical process is made in the subsequent discussion, the objections to this theory are not restated.

Aluminum alloys. Stress corrosion cracking of 96 percent aluminum-4 percent copper and 93 percent aluminum-7 percent magnesium alloys in sodium chloride containing a little sodium bicarbonate proceeds in alternating steps of instantaneous fracture and corrosion. Proof of the instantaneous nature of the mechanical step was obtained from the sudden changes of the electrochemical potential and also from the sound generated during such changes. The present observations agree with reports[5,6,7] that crack propagation in these alloys involves the rapid destruction of mechanically weak "bridges" and the slower penetration through mechanically resistant areas by electrochemical corrosion. It should be pointed out that the present results do not show the nature or the size of the mechanical steps: thus, each step could have been the formation of a new crack at the surface of the specimen or the propagation of an existing one within the specimen.

In case of failure without any steps, it is tentatively suggested that the very first jump was long enough to cause complete failure, although no experimental proof is available. An alternative explanation, of course, is that the mechanical fracture steps are purely secondary, and that the metal would, in any case, fail by stress corrosion cracking even in their absence. In view of the existing reports, however, this explanation is probably of less importance.

The results reported above served very well to demonstrate the sensitivity of the instruments which are being used in other experiments.

Magnesium-base alloy AM-57S-H. The failure of this material by stress corrosion cracking in 3.5 percent sodium chloride containing 2 percent of either potassium chromate or potassium dichromate is extremely rapid. Mears, Brown and Dix[7] reported that failure was transgranular in the first solution and intergranular in the second, so that the present results refer to both types of cracking.

Cracking apparently starts almost immediately after the specimen is immersed, since cracks can be seen at a very early stage. Throughout the period of cracking before the final catastrophic rupture, no evidence was found of any mechanical steps, since the potential curves were smooth, and no sound could be heard over the acoustic system. It is therefore concluded that the mechanism of stress corrosion cracking of the alloy is entirely electrochemical without mechanical steps, except when the final violent parting occurs.

An interesting observation was that the slopes of the potential curves were opposite for specimens in the two solu-

tions, as shown in Figure 26. These curves indicate that the alloy becomes increasingly active in the solution containing chromate, while, in the presence of dichromate, the potential never moves in the active direction, up to the point of final failure.

Mild steel. The mechanism of crack propagation in mild steel is intermediate between that of stainless steel, which showed no mechanical fracture, and that of the two aluminum alloys which consisted of alternating instantaneous and slow steps. Thus, the potential changes during cracking were gradual for most of the time, but every now and then a very rapid change would occur, showing a relatively sudden formation of fresh surface.

These changes, however, were never instantaneous, occurring over periods ranging from 10 or 15 seconds to almost 2 minutes, as shown graphically in Figure 22. They do not resemble the shape of the curve obtained at sudden fracture, Figure 23, although they do represent a change from the experimental observations for stainless steel, where crack propagation was gradual throughout the period of failure. Furthermore, the acoustic tests gave no indication of the generation of sound during the cracking process. This confirms the absence of steps other than extremely small ones of instantaneous physical parting in the metal.

It is concluded that mild steel cracks in nitrate solutions in a discontinuous fashion, in which there are alternating steps of slow and fast propagation of the cracks. The slow step is probably entirely electrochemical, while the rapid step could consist either of a very fast removal of metal, along the cracking path, by corrosion, or of a very slow mechanical parting of the alloy, which could probably also be noiseless.

Conclusions

Of the materials examined, sudden fracture steps occur only during stress corrosion crack propagation in the two aluminum-base alloys. The advance of cracks in stainless steel, mild steel and a magnesium-base alloy was relatively slow, and in all cases consistant with an electrochemical theory. In supporting this theory, however, it should be stated that there is no exclusive proof of any one of the existing theories which are based on this general mechanism. Furthermore, extremely small mechanical fracture steps, which may escape detection, might also contribute to failure.

It should also be pointed out that the data do not exclude an adsorption effect which could lower the free energy of the surfaces of a crack sufficiently to cause a spontaneous parting in the metal under stress; a feature of the latter mechanism, however, must be that it is under control of a step slow enough to prevent brittle failure. Such a slow step could perhaps be the penetration of liquid to the base of the fissure and the setting up of the required adsorbed layer on the surface.

Another feature of the adsorption mechanism, if it exists, must be that it is a slow process which can be stopped by the application of small, direct cathodic currents to the metals. A feature of the electrochemical mechanism, on the other hand, must be that the corrosion reactions are sustained at high anodic current densities in spite of the possible accumulation of soluble corrosion products in the cracks, and in spite of the restricting dimensions of the cracks. It is possible that the over-all mechanism of stress corrosion cracking may consist of two or more simultaneously active processes.

Acknowledgments

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The author wishes to thank G. R. McGraw and C. J. Dorsch, of the Westinghouse Research Metallurgy Department, for assisting in carrying out the experimental work.

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Hydrogen Permeation Through Metals, Alloys and Oxides at Elevated Temperatures*

By C. L. HUFFINE and J. M. WILLIAMS

Abstract

Permeation rates of hydrogen through AISI Type 446 stainless steel and an iron-chromium-aluminum alloy (20 percent Cr, 5 percent Al, balance Fe) were determined to 2150 F under various conditions of surface oxidation. The presence of a continuous oxide film resulted in a thousand fold reduction in permeation rate over that through the unoxidized metal at elevated temperatures. Under conditions in which the oxide could not be replenished, its barrier effect was largely destroyed through reduction of the oxide by the emerging hydrogen. 3.3.6

Introduction

PERMEATION OF hydrogen through metals at elevated temperatures is of interest commercially both from the standpoint of containment of the gas and for its effect on the properties of the metal. In addition, the study of the permeation process in cases where surface films of oxide are involved gives valuable insight into the nature of these films.

Many investigations have been made of the permeation of clean metals,[1] and in all cases diffusion of a dissociated hydrogen atom was postulated as the rate determining mechanism from the dependence of the permeation rate on the square root of the hydrogen pressure. A general relation correlating all parameters for such cases has been concisely stated by Dushman:[2]

$$R = \frac{k}{t}\left(P_1^{1/2} - P_2^{1/2} \right) e^{-b/T}$$

where R is the absolute permeation rate, k and b are constants, t is the thickness, P_1 and P_2 are the upstream and downstream pressures, and T is the absolute temperature.

Most investigations of permeation rate have been plagued by contamination of specimen surfaces by gas-borne impurities, particularly oxygen and nitrogen. This contamination universally resulted in lowering of permeation rates. In only one reported case, however, has any extensive attempt been made to evaluate the effect of an oxide film on the permeation rate through a metal. Flint[3] prepared oxide films on AISI Type 347 stainless steel by treatment in wet hydrogen and observed reductions in permeation rate of as much as 400-fold over the rate through the clean metal under identical test conditions. These tests were transient in nature, and rate increases were observed with time as the oxide film was reduced.

The present work was concerned with evaluation of the permeation properties of two oxidation resistant high temperature alloys, AISI Type 446 stainless steel (nominal composition 25 percent Cr, balance Fe) and an iron-chromium-aluminum alloy (nominal composition 20 percent Cr, 5 percent Al, balance Fe). The work was carried out in three phases:

1. Measurement of permeation rates through clean (i.e., unoxidized) metal sheet.

2. Measurement of rates through metal sheet initially oxidized on the surface through which hydrogen emerged, but measured under conditions such that the oxide film was not replenished as permeation proceeded (i.e., "transient" test similar to that of Flint, above.)

3. Measurement of rates through metal sheet under conditions where the surface through which hydrogen emerged was continuously exposed to an oxidizing atmosphere during the test.

The methods and results of each phase are presented separately in the following sections.

Huffine

Williams

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Permeation of Clean Metals

Procedure

As the materials of interest were available only in the form of 0.015" thick sheet stock, the specimen container (Figure 1) was designed for use with a membrane specimen. The membranes were cleaned by abrading and sealed between the heavy walled cups by inert arc welding in an argon filled chamber. The specimen was helium leak tested on both sides.

For detection and measurement of the hydrogen permeating the membrane, a metered stream of purified argon was directed over the membrane and the resulting hydrogen-argon mixture was continuously compared with a reference stream of the same argon in a Gow-Mac thermal conductivity gas analysis unit.

Because of the 10 to 1 ratio of conductivities of hydrogen and argon, this instrument gave extremely high sensitivity, and measured permeation rates were estimated to be accurate to ±2 percent. Figure 2 shows the complete flow diagram for the permeation measurements. Gases were purified by passage over calcium hydride at 1300 F and zirconium turnings at 1850 F.

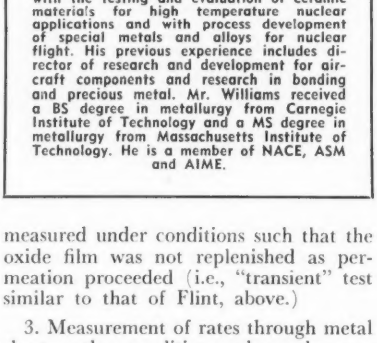

Figure 1—Sketch of diaphragm permeability specimen showing method of welding diaphragm between heavy-walled 310 stainless steel cups.

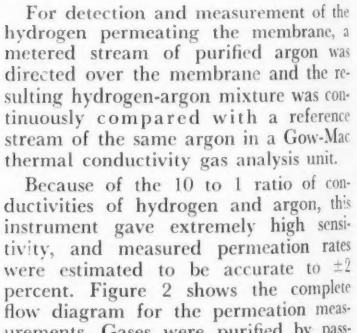

Figure 2—Apparatus used in permeability measurements with diaphragm specimens.

★ Submitted for publication December 10, 1959.

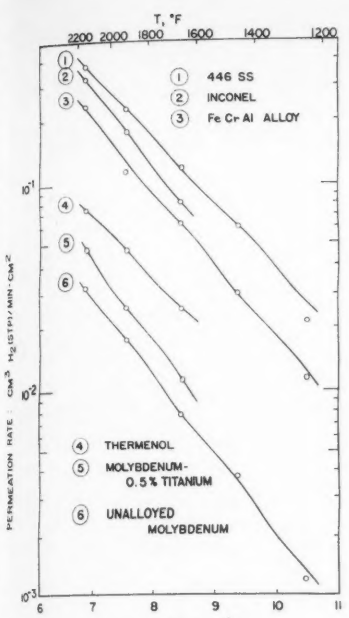

Figure 3—Hydrogen permeation rates through unoxidized metals and alloys as function of temperature. All specimens 0.015 inch thickness. Hydrogen pressure differential 810 mm mercury.

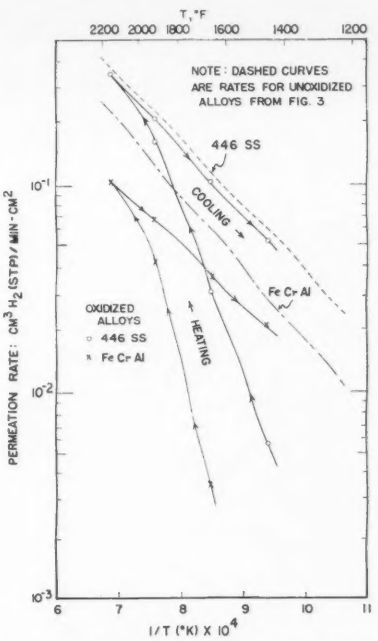

Figure 4—Hydrogen permeation rates through alloys initially oxidized on downstream side. Permeation measures without further access to oxygen. All specimens 0.015 inch initial thickness. Hydrogen pressure differential 810 mm mercury.

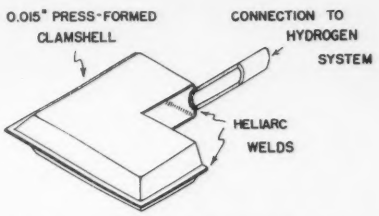

Figure 5—Sketch of clamshell permeability specimen showing method of welding to connection tube.

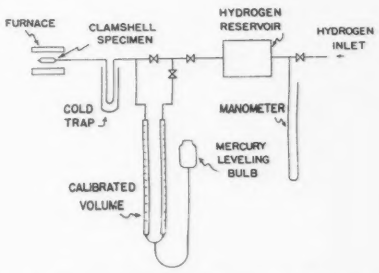

Figure 6—Apparatus used in permeability measurements with clamshell specimens.

The entire system was purged for at least 12 hours before each run with purified argon. The analysis unit was checked periodically against a standard gas mixture.

The general test pattern was to heat the specimen quickly to a specific temperature and hold it at this level until a steady permeation rate was obtained. The temperature would then be increased to the next level and this process repeated until the desired maximum temperature was reached. Similar plateaus would then be established as the temperature was reduced.

Results were calculated in cc H_2 (STP)/min/cm.^{2} All tests were made with 0.015" thick membranes and with an 810 mm Hg absolute hydrogen pressure on the hydrogen side of the membrane. Since the small amount of hydrogen permeating the membrane was continuously removed by the argon stream, the downstream partial hydrogen pressure was essentially zero, and the pressure differential was therefore 810 mm Hg.

Results

Results are shown in Figure 3 plotted as the conventional Arrhenius exponential temperature relation. Plotted points for 446 SS and FeCrAl are the averages for 4 different specimens. Values obtained in single runs on specimens of Inconel (nominal composition 16 percent Cr, 7 percent Fe, balance Ni), Thermenol (nominal composition 15 percent Al, 3 percent Mo, balance Fe), unalloyed molybdenum, and a molybdenum-0.5 percent titanium alloy are also shown.

Discussion

Comparison of the results on 446 SS, FeCrAl, and Thermenol indicates a pronounced decrease in permeation rate with increase in aluminum content of the alloy. This may be the result of decreased diffusion due to decreased hydrogen solubility, but is more probably indicative that the residual oxide films on the specimens were more tenacious at higher aluminum levels. All specimens appeared as bright after testing as before, but the presence of an extremely thin oxide film was inescapable in the specimen preparation. This film probably remained on the surfaces throughout the tests. The gas purification train was apparently effective in removing trace impurities, since no change in steady state permeation rates was observed over long periods of time (i.e., 4 to 6 hours).

Reproducibility of results with different specimens of the same alloy was acceptable, the maximum spread in measured permeation rates at a given temperature being ±15 percent.

The permeation rate observed at a given temperature as temperature decreased was generally about 20 percent lower than that observed at the same temperature on the initial increasing temperature portion of the run. This difference decreased as the sample was run through several cycles of temperature change. This effect has been observed in most permeation investigations, and is usually attributed to "poisoning" of the specimen surfaces by gas-borne impurities. These investigations, however, usually observed a decline in rate with time under constant temperature conditions, and this was not observed in the present tests. The specimens were initially prepared from annealed stock, but it was certain that considerable recrystallization and grain growth occurred at the elevated temperatures of the test. The change in permeation may, therefore, be related to this rather than to the usual poisoning effect.

Permeation of Initially Oxidized Metals

Procedure

To study the effect of pre-oxidizing the metal surface, air was passed through the downstream or "argon" side of the sample cell while the cell was heated to 1900 F. On cooling, the argon system was reconnected and the permeation run made in the usual way. One capsule containing a 446 SS diaphragm was cut open after the oxidation step for examination of the oxidized surface. The surface was uniformly blackened and the oxide appeared remarkably smooth and free from any evidence of flaking. Metallographic examination showed only a thin film of oxide (estimated at 15 micron thickness) with no evidence of intergranular penetration or other effect on the metal substrate.

Results

The results obtained on 446 SS and the FeCrAl alloy were generally the same. In each case, the permeation rate was found to be quite low as compared with that of the clean metal, but the difference became less as the temperature was increased. On decreasing the temperature the rates paralleled the values for clean metal, but were still somewhat lower. A typical run for each material is shown in Figure 4.

Examination of the diaphragms after the permeation measurement showed essentially the original bright surface on the 446 SS and a gray film on the FeCrAl.

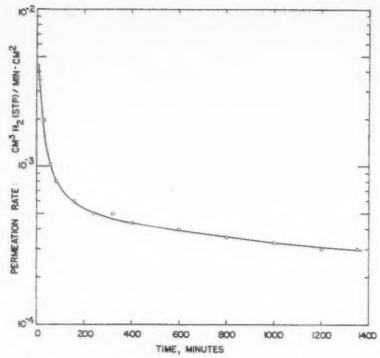

Figure 7—Permeation rate as function of time for previously unoxidized Fe-Cr-Al clamshell specimen heated rapidly to 2000 F and maintained at temperature. Initial specimen thickness: 0.015 inch; hydrogen pressure: 810 mm mercury absolute.

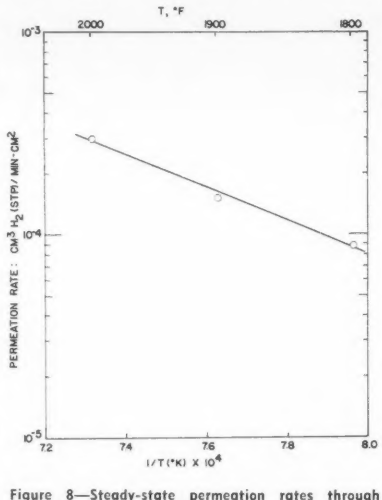

Figure 8—Steady-state permeation rates through Fe-Cr-Al clamshell specimens as function of temperature. Initial specimen thickness: 0.015 inch; hydrogen pressure: 810 mm mercury absolute.

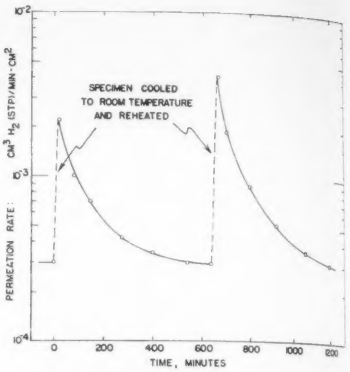

Figure 9—Effect of rapid temperature cycles on permeation rate through Fe-Cr-Al clamshell specimen at 2000 F. Initial specimen thickness: 0.015 inch; hydrogen pressure: 810 mm mercury absolute.

Discussion

The results of these tests seem consistent, and indicate that an oxide film reduces permeation rates to an appreciable extent. In those cases in which the film is reducible by hydrogen, however, the rate increases as the film is removed, and returns to a value approximating that of clean metal. Even when the film is not completely reducible, as is the case with FeCrAl, a partial reduction is apparently accomplished with an accompanying increase in premeation rate.

Permeation of Continuously Oxidized Metals

Procedure

For study of permeation under conditions in which the downstream side of the membrane was continuously exposed to air, a different apparatus was employed. The membrane was formed into a "Clamshell" capsule as shown in Figure 5. This was sealed to a calibrated chamber from which hydrogen could be supplied at constant pressure, the change in volume with time giving a measure of the rate at which hydrogen permeated the capsule. This apparatus is shown schematically in Figure 6. The measurement of permeation rates by this means was somewhat less accurate than that previously employed, but was adequate for the intended purpose.

Permeation runs with this apparatus were made by inserting the capsule in the furnace, which was controlled at the desired temperature. The capsule reached this temperature within ten minutes, and continuous measurements of permeation rate were then made for desired periods of time at constant temperature. In some tests, the specimen was cycled to room temperature by removing from the furnace and reinserting.

Results

Permeation rates on a new unoxidized specimen were initially high, but showed a rapid decrease with time at constant temperature. This is shown in Figure 7. This declining rate, which tended to approach a constant value, was quite evidently the result of the buildup of the oxide layer on the outer surface of the capsule. When the oxidation rate reached a steady value, the permeation also became constant. Figure 8 is the Arrhenius plot of the "steady state" values for continuously oxidized FeCrAl at the temperatures tested. Steady state permeation rates below 1800 F were too low for accurate measurement by the method employed.

When a capsule which had reached steady state was cycled to room temperature and back to the original temperature, the permeation rate showed a sharp increase followed by a slow decline to the original steady state value. This is illustrated in Figure 9.

Discussion

The steady state permeation rate through the oxidized FeCrAl was seen to be some three orders of magnitude lower than that through the clean metal at the same temperature. Although permeation data alone are insufficient to permit proof of a mechanism, a rational explanation of the results can be made with the presumption that the rate limiting process is one of diffusion in each case, and that the rate of diffusion through the continuous oxide film is much lower than that through the metal.

The behavior of the permeation rate on cycling was interpreted as evidence that the continuous oxide film was disrupted by the thermal stresses involved in the cooling and reheating, thus permitting increased passage of hydrogen until the film was healed by re-oxidation.

Conclusions

The formation of a continuous oxide film on a metal surface results in a thousand-fold reduction in the rate of hydrogen permeation at elevated temperatures. While not conclusively proved, the evidence indicates that this reduction in rate is the result of comparatively slow diffusion through the oxide layer. Thermal shocks, or other stresses which tend to destroy the continuity of the oxide film result in greatly increased permeation rates, which slowly return to the original value as the film is healed by re-oxidation.

Under conditions where the oxygen content of the film cannot be replenished, its effectiveness as a barrier decreases due to complete or partial reduction by the permeating hydrogen.

Study of hydrogen permeation under various conditions affords valuable insight into the nature of oxidation processes and deserves greater consideration as a tool in the study of high temperature corrosion of metals.

Acknowledgment

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Compositional Effects in the Corrosion Of Type 347 and 316 Stainless Steel In Chemical Environments*

By C. P. DILLON

Abstract

Statistical analysis indicates that some improvement in corrosion resistance of Type 347 stainless steel, in so far as this is indicated by the Huey Test, can be effected by tightening control of the compositional limits. The major improvement is effected by limiting the maximum silicon content; the chromium content and the columbium: carbon ratio are next in importance.

In practice, adequate quality control is probably established by the qualification test itself, since variables other than composition significantly affect the corrosion resistance of the alloy in boiling 65 percent nitric acid. Statistical analysis of both qualification tests and field corrosion tests of chromium-nickel-molybdenum stainless steel indicates that the influence of various compositional elements varies with environment. A compositional range that is best for one type of exposure is not the optimum composition for another. Performance of annealed material (or of sensitized extra low carbon material) in qualification tests cannot be used to indicate quality as to general corrosion resistance in other environments.

In practice, the effect of variations of composition within the nominal ASME range do not significantly affect corrosion resistance. In isolated cases where performance is affected, this must be determined empirically. 6.2.5

Introduction

A NUMBER of generalizations may be made concerning the influence of individual alloying elements on the corrosion resistance of stainless steels. In a general way, corrosion resistance increases with increased chromium content. An increase in carbon content is considered detrimental (although primarily in regard to intergranular, rather than uniform, corrosion). Additions of molybdenum to the basic 18-8 chromium-nickel steel increase resistance to chlorides and to reducing environments in general. It should be noted, however, that it is one thing to generalize about beneficial or adverse effects, and quite another to state whether practical differences will be observed within certain specific compositional ranges or in specific environments.

It is more difficult to determine the effects of variations in concentration of individual elements when specific instances are considered. Indeed, variations in elements other than chromium are likely to cause quite variable effects. Even increases in chromium may indirectly lead to a diminution of resistance unless the austenite balance is maintained by increasing the concentration of such austenite-forming elements as nickel, manganese, nitrogen, and carbon.

Obviously, the beneficial effects of increased chromium will be offset in environments in which the required corresponding increase in austenitizing components has an adverse effect.

There are certain specific instances of benefits from increased alloy content which have perhaps mistakenly occasioned unwarranted generalizations. For example, Rhodin[1] has shown an increased resistance from silicon content in ferric chloride solutions. A *minimum* molybdenum content of the order of 2.25 percent has been frequently cited for certain acetic acid or phosphoric acid services.

The question as to which elements, and how much, affect resistance (and to what extent) is important in writing materials specifications and in the selection of alloys for chemical processes. It must be borne in mind that the stipulated composition must be sound from the metallurgical aspect and compatible with mill and shop practices. If different from commercial specifications, it should be *significantly* better at least in the application under consideration.

Another practical question is whether, in terms of general corrosion resistance, alloying for optimum performance in a standard qualification test (which is primarily intended to study resistance to intergranular corrosion) actually improves the overall resistance. While the author feels it is fallacious to infer from qualification tests resistance other than to intergranular corrosion, this is a common aspect of their use by many engineers not fully cognizant of the background and purpose of such tests.

It was considered desirable to investigate these matters as fully as possible with the data available and to conduct a limited amount of experimentation.

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About the Author

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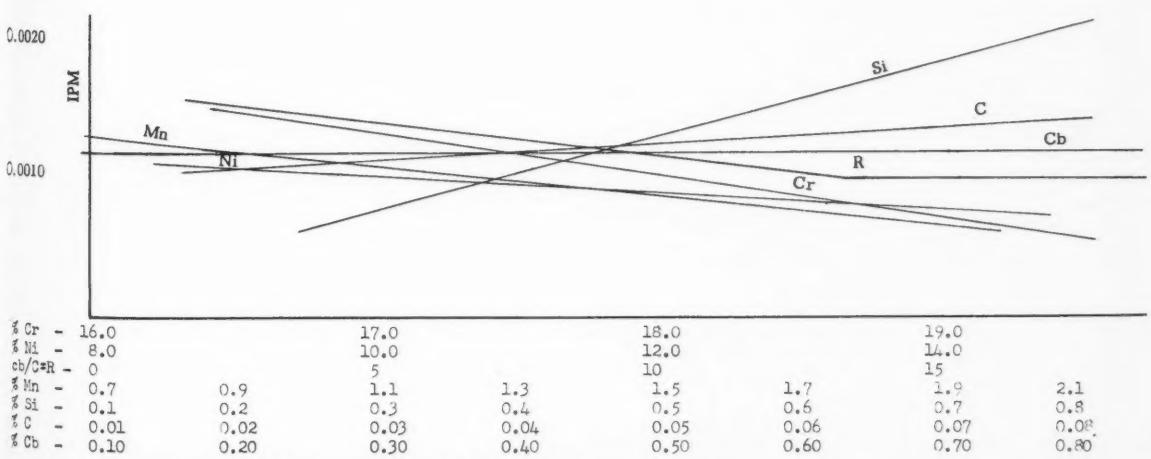

Figure 1—Composition of Type 347 stainless steel vs corrosion rates in Huey test.

Procedures

Actual data on specific heats of both columbium-stabilized and molybdenum-bearing stainless steel are available in the literature. It is surprising, however, to find how infrequently complete chemical analyses are given with the corrosion data. All too frequently the analyses are incomplete, or even non-existent with only a nominal composition being given.

In addition to the literature data, analyses and corrosion data were available from the Union Carbide Metals Research Laboratory. Most qualification tests for material used by divisions of Union Carbide Corporation have, until very recently, been conducted there.

Additional data, particularly as to field corrosion tests, were obtained by a definite program in the Union Carbide Chemicals Company plants at Texas City, Texas, Institute, West Virginia and South Charleston, West Virginia. These tests were used primarily to compare the resistance of several heats of chromium-nickel-molybdenum stainless steels of quite variable composition.

In evaluating the effects of individual alloying elements on corrosion resistance to both qualification tests and to process environments, a graphical technique of multiple correlation[2] was employed to determine to what extent the corrosion behavior could be explained in terms of composition. These techniques result in a series of curves, each of which is essentially the partial derivative of the dependent variables (elements of composition). Mathematically then, each curve is the effect of that element of the composition on corrosion rate if all other elements are held constant. The important thing to note on each curve is the magnitude and direction of its slope. In this study, negative slopes are desirable and the steeper the slope, the stronger is the effect of the element, and the greater the necessity for control.

Chromium-Nickel-Columbium Steels

The investigation of Type 347 stainless steel was confined to a consideration of the possible necessity for composition requirements more stringent than those for the commerical alloy. The use of Type 347 is restricted primarily to services above 800 F in which there are simultaneously, subsequently, or intermittently present agents specific for intergranular

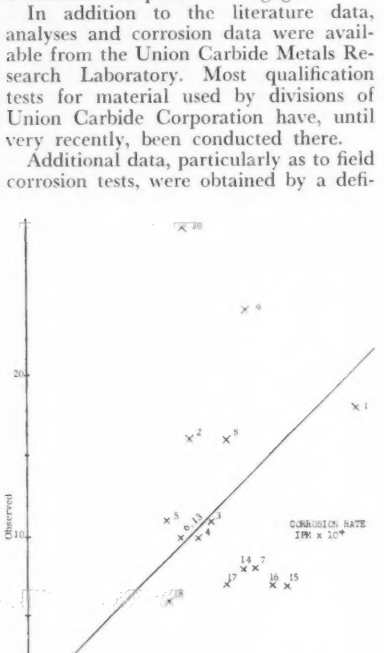

Figure 2—Graphical correlation of calculated vs observed corrosion rates for Type 347 stainless steel in Huey test.

TABLE 1—Composition Limits for Type 347

Element	ASTM A-167	ASTM A-240	PVM-347
Carbon	0.10 Max.	0.08 Max.	0.07 Max.
Manganese	1.5 Max.	2.5 Max.	1.25 Min.
Silicon	1.0 Max.	0.85 Max.	0.75 Max.
Chromium	18.0 Min.	17.0 Min.	18—20
Nickel	9—12	9.5 Min.	10—12
Columbium	10 x C Min.	10 x C, 1.0 Max.	10 x C, 1.0 Max.

Heat No.	C	Mn	Si	Ni	Cr	Cb	R*	IPM**
1[1]	0.060	1.25	0.75	10.69	18.32	0.74	12.2	0.0018
2[1]	0.020	1.26	0.38	11.00	17.14	0.33	16.5	0.0016
3[1]	0.026	1.33	0.47	11.32	17.47	0.48	18.4	0.0011
4[1]	0.027	1.15	0.37	12.00	17.61	0.30	11.1	0.0011
5[2]	0.065	1.38	0.39	10.98	18.74	0.75	11.5	0.0011
6[2]	0.022	1.11	0.46	11.75	18.36	0.42	19.1	0.0010
7[2]	0.007	0.72	0.66	15.04	18.41	0.89	127	0.0016
8[3]	0.077	0.96	0.47	10.34	18.80	1.19	15.4	0.0016
9[3]	0.074	1.09	0.52	12.14	18.60	0.76	10.3	0.0024
10[4]	0.08	1.37	0.39	11.23	18.48	1.02	12.7	0.0029
11[4]	0.10	...	....	8.56	18.49	0.44	4.4	0.0022
12[3]	0.06			9.45	18.86	0.75	12.5	0.0007
13[5]	0.06	0.50	0.27	9.92	18.39	0.72	12.0	0.0010
14[5]	0.06	0.65	0.49	9.45	18.86	0.74	12.3	0.0008***
15[5]	0.07	0.99	0.45	10.10	17.66	0.54	7.7	0.0007***
16[5]	0.07	0.99	0.44	10.47	17.53	0.87	12.4	0.0007***
17[5]	0.07	1.68	0.46	10.01	17.99	0.84	12.0	0.0007***
18[6]	0.07	2.08	0.56	10.55	19.21	0.96	13.7	0.0006***

* R = Cb/C
** Sensitized 1 hour at 1250 F
*** Air Cooled from 1075 C
[1] Buck, Phillips, Heger and Queneau
[2] Binder and Brown
[3] Teeple
[4] Comstock
[5] Franks, 2-27-39
[6] Franks, 7-13-58

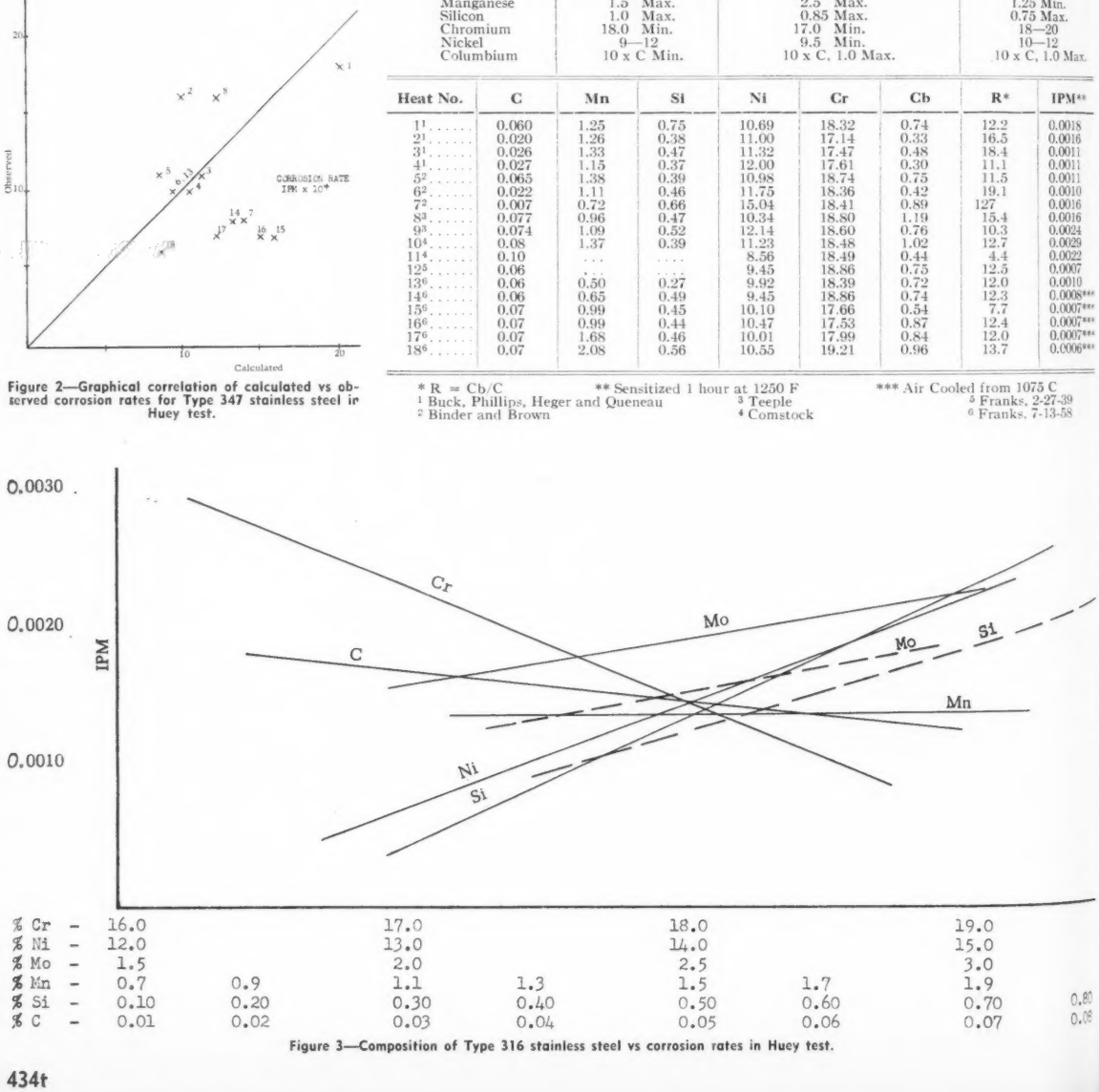

Figure 3—Composition of Type 316 stainless steel vs corrosion rates in Huey test.

corrosion. Otherwise, extra-low carbon material (Type 304L) is employed unless advantage can accrue from the higher mechanical strength of Type 347.

The determination of the possible need for a stabilized or extra-low carbon grade is established by tests of annealed and sensitized regular carbon Type 304, using field tests wherever possible. Consequently, primary concern is with demonstrating that the material bought to specifications for 347 or 304L is, in fact, demonstrably resistant to intergranular corrosion.

Data for resistance of 18 heats of Type 347 in the "sensitized" condition were selected from sources available.[3, 4, 5, 6, 7, 8] The composition of the alloys are given in Table 1. Upon examination by the statistical method referred to, a set of curves was obtained which define the specific influence of the individual alloying elements (Figure 1).

Since the curves are based upon a limited sampling, no purely quantitative interpretation should be placed on them. However, they are believed to be reliable in regard to trend and order of magnitude within the compositional limits explored.

The following conclusions may be drawn from examination of the curves derived:

1. Chromium, manganese and nickel (in descending order of importance) are beneficial in minimizing corrosion rates in the Huey Test (ASTM A-262).

2. The ratio of columbium to carbon has a beneficial effect, reaching a maximum in the vicinity of R = 13.5, after which a further increase is of no effect.

3. Carbon and silicon have an adverse effect, the latter being more significant.

The derived curves were used to predict corrosion rates for material falling within the ASTM A-167 and A-240 specifications and for a proposed restricted composition (PVM 347). The best and worst compositions anticipated within these specifications are given in Table 2. The corresponding calculated corrosion rates are given in Table 3.

It will be observed that material falling within the A-167 and A-240 requirements can readily fail the stipulated maximum corrosion rate of 0.0020 inch per month for sensitized material. The proposed composition would almost eliminate the failures, in so far as they are influenced by composition alone.

The arithmetical verification of the curves is given in Table 4 and plotted in Figure 2. The wide deviation of points 9 and 10 as regards calculated versus observed rates is probably due to effects other than composition. The low points for heats 14 to 17 are probably due to insufficient sensitization in that these particular heats were "air-cooled" from 1075 C rather than sensitized for one hour at 1200-1250 F as were the others.

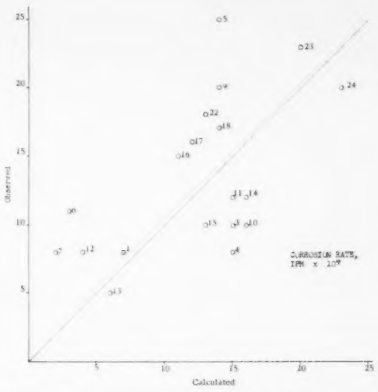

Figure 4—Graphical correlation of calculated vs observed corrosion rates for Type 316 stainless steel in Huey test.

In any event, although the curves define the effects of composition, it is evident from the poor correlation that other factors very strongly affect corrosion rates in the Huey Test. Among the known possible factors which may be involved in the poor correlation are the following:

1. Improper annealing during manufacture.

TABLE 2—Calculated Maximum and Minimum Type 347 Alloy Composition

	ASTM-A167		ASTM-A240		PVM-347	
Element	Best	Worst	Best	Worst	Best	Worst
Carbon	0.05	0.10	0.05	0.08	0.05	0.07
Manganese	1.5	0.50	2.5	0.50	2.5	1.25
Silicon	0.30	1.00	0.30	0.85	0.30	0.75
Chromium	20	18	19	17	20	18
Nickel	12	9	13	9.5	12	10
Columbium	1.0	0.7	1.0	0.80	1.0	0.7
Cb/C	20	10	20	10	20	10

TABLE 3—Calculated Maximum and Minimum Corrosion Rate (IPM) of Alloys in Table 2

	f(C)	F(Mn)	f(Si)	f(Ni)	f(Cr)	f(Cb)	f(R)	*S	S-a**
A-167:									
Best	13	11	7.9	10	4.2	12	10	68	0
Worst	15	14	26.0	11	10.5	12	12	100.5	32.3
A-240:									
Best	14.5	6.7	7.9	9.5	7.3	12	10	67.9	0
Worst	16	14	22.8	11	13.7	12	12	101.5	33.3
PVM 347:									
Best	14	6.7	7.9	10	4.2	12	10	64.8	0
Worst	16	11.3	20	10.7	10.5	12	12	92.5	24.3

* Sum of factors.
** S-a = Calculated Corrosion Rate, IPM x 10^4

TABLE 4—Verification Data and Factors for Figure 2

Heat No.	f(R)	f(Cr)	f(Ni)	F(Mn)	f(Si)	f(C)	F(Cb)	S[1]	S-a[2]	Obs.[3]
1	10.5	9.5	10.4	11.8	21.0	13.4	12.0	88.6	20.4	18
2	10.0	13.2	10.3	11.8	10.1	11.4	12.0	78.8	10.6	16
3	10.0	12.2	10.2	10.7	12.7	11.7	12.0	79.5	11.3	11
4	11.0	11.8	10.0	12.1	9.9	11.9	12.0	78.7	10.5	10
5	10.7	8.2	10.3	11.4	10.5	13.7	12.0	76.8	8.6	11
6	10.0	9.3	10.0	12.5	12.4	11.7	12.0	77.9	9.7	10
7	10.0	9.3	8.7	13.6	17.8	10.8	12.0	82.2	14.0	8
8	10.0	8.0	10.6	12.9	12.7	14.3	12.0	80.5	12.3	16
9	11.5	8.6	9.9	12.2	13.4	14.1	12.0	81.7	13.5	24
10	10.3	8.9	10.2	11.4	10.5	14.5	12.0	77.8	9.6	29
11	14.8	8.9	11.3	....	....	15.5	12.0	62.5	....	....
12	10.5	7.8	10.9	....	....	13.4	12.0	54.6	....	....
13	10.4	9.3	11.2	14.2	7.2	13.4	12.0	77.7	9.5	10
14	10.5	7.8	10.9	13.7	13.2	13.4	12.0	81.5	13.3	8
15	13.0	11.8	10.7	12.6	12.2	13.9	13.0	86.2	16.0	7
16	10.4	12.0	10.5	12.6	11.9	13.9	12.0	83.3	15.1	7
17	10.7	10.5	10.7	10.5	12.3	13.9	12.0	80.6	12.4	7
18	10.0	6.5	10.4	9.3	15.0	13.9	12.0	77.1	8.9	6
						Average "S" =		80.656		12.4
								— 12.4		
								a = 68.2		

[1] S = Sum of Factors.
[2] S-a = Calculated Corrosion Rate, IPM x 10^4.
[3] Observed Corrosion Rate, IPM x 10^4.

TABLE 5—Composition of 24 Heats of Type 316

Heat No.	C	Cr	Ni	Mo	Mn	Si
1	0.06	16.56	13.05	2.30	1.50	0.43
2	0.043	17.99	12.38	....	1.88	0.68
3	0.020	18.46	13.53	2.77	1.82	0.65
4	0.021	17.74	13.54	2.63	1.66	0.54
5	0.023	17.88	13.50	2.59	1.97	0.60
6	0.025	18.27	13.33	2.70	1.63	0.43
7	0.010	18.12	13.53	....	1.43	0.70
8	0.029	17.43	13.56	2.28	1.84	0.56
9	0.020	17.45	13.26	2.18	1.85	0.56
10	0.024	17.55	13.57	2.57	1.66	0.55
11	0.025	17.01	13.55	2.33	1.29	0.47
12	0.027	17.28	13.40	2.45	1.80	0.29
13	0.030	17.22	13.65	2.38	1.56	0.32
14	0.026	17.33	13.39	2.63	1.48	0.53
15	0.028	17.19	13.41	2.33	1.60	0.52
16	0.025	17.30	13.44	2.27	1.75	0.49
17	0.026	17.88	13.87	2.22	1.68	0.57
18	0.025	17.01	13.55	2.33	1.29	0.47
19	0.027	17.22	13.55	2.40	1.47	0.44
20	0.054	17.98	13.04	2.21	1.67	....
21	0.053	18.65	12.77	2.23	1.22	....
22	0.030	16.78	13.82	2.30	1.41	0.37
23	0.026	17.18	14.92	2.13	1.54	0.45
24	0.028	17.08	14.96	2.18	1.60	0.48

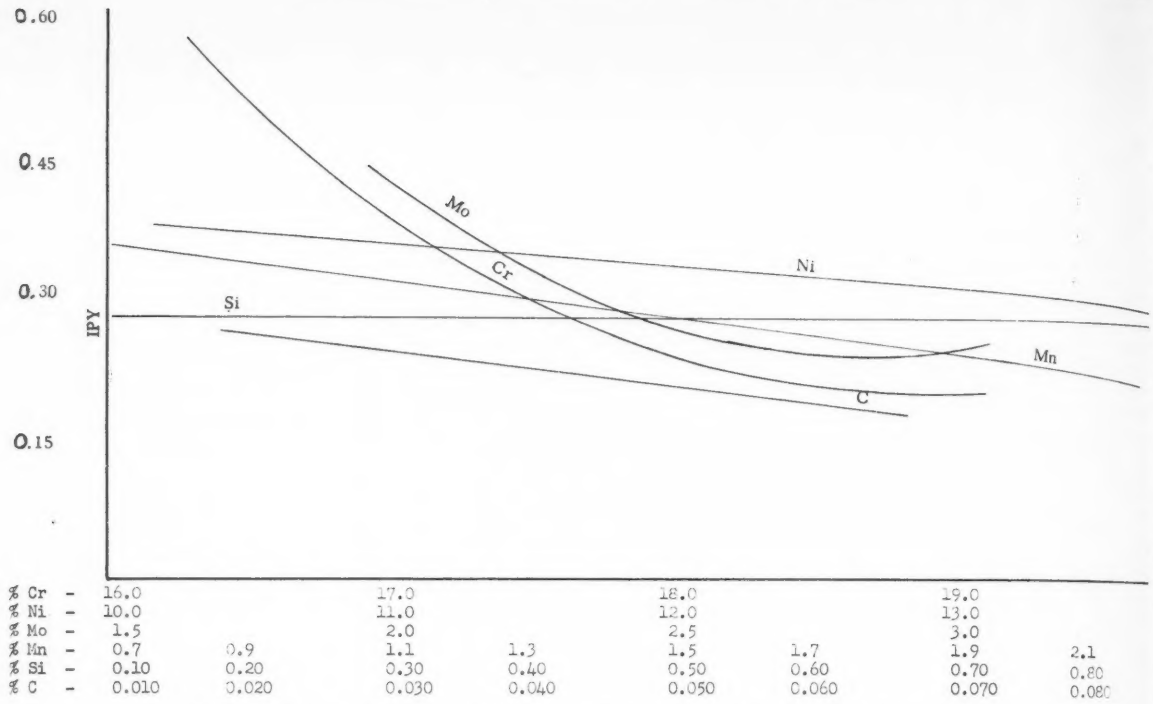

Figure 5—Composition of Type 316 stainless steel vs corrosion rates in nitric-hydrofluoric acid evaluation test.

TABLE 6—Verification of Curves for Type 316 in Huey Test

Heat No.	f(C)	f(Cr)	f(Ni)	f(Mo)	f(Mn)	f(Si)	S	·f'o*	fo
1	0.0011	0.0025	0.0007	0.0017	0.0013	0.0010	0.0083	0.0007	0.0008
2	0.0014	0.0014	0.0003	.....	0.0013	0.0021	0.0065	.....	.....
3	0.0017	0.0010	0.0011	0.0020	0.0013	0.0020	0.0091	0.0015	0.0010
4	0.0017	0.0016	0.0011	0.0019	0.0013	0.0015	0.0091	0.0015	0.0008
5	0.0017	0.0014	0.0010	0.0019	0.0013	0.0017	0.0090	0.0014	0.0025
6	0.0016	0.0011	0.0009	0.0020	0.0013	0.0010	0.0079	0.0003	0.0011
7	0.0019	0.0013	0.0011	.....	0.0013	0.0022	0.0078	0.0002	0.0008
8	0.0016	0.0018	0.0010	0.0017	0.0013	0.0016	0.0090	.....	.....
9	0.0017	0.0018	0.0009	0.0016	0.0013	0.0016	0.0089	0.0014	0.0020
10	0.0017	0.0017	0.0010	0.0019	0.0013	0.0016	0.0092	0.0016	0.0010
11	0.0016	0.0022	0.0011	0.0017	0.0013	0.0012	0.0091	0.0015	0.0012
12	0.0016	0.0019	0.0010	0.0018	0.0013	0.0004	0.0080	0.0004	0.0008
13	0.0016	0.0020	0.0010	0.0017	0.0013	0.0005	0.0081	0.0005	0.0006
14	0.0016	0.0019	0.0009	0.0019	0.0013	0.0015	0.0091	0.0016	0.0012
15	0.0016	0.0020	0.0009	0.0017	0.0013	0.0014	0.0089	0.0013	0.0010
16	0.0016	0.0019	0.0009	0.0017	0.0013	0.0013	0.0087	0.0011	0.0015
17	0.0016	0.0014	0.0013	0.0016	0.0013	0.0016	0.0088	0.0012	0.0016
18	0.0016	0.0022	0.0010	0.0017	0.0013	0.0012	0.0090	0.0014	0.0017
19	0.0016	0.0020	0.0010	0.0017	0.0013	0.0010	0.0086	.....	.....
20	0.0012	0.0014	0.0007	0.0016	0.0013	.....	0.0062	.....	.....
21	0.0012	0.0008	0.0005	0.0016	0.0013	.....	0.0054	.....	.....
22	0.0016	0.0024	0.0012	0.0017	0.0013	0.0007	0.0089	0.0013	0.0018
23	0.0016	0.0020	0.0020	0.0016	0.0013	0.0011	0.0096	0.0020	0.0023
24	0.0016	0.0021	0.0020	0.0016	0.0013	0.0012	0.0098	0.0022	0.0020
						Total**	0.1854		0.0257
						Average	0.0089		0.0013
									—0.0089
									a— 0.0076

*f'o = S+a where a = fo (Avg.)—S (Avg.)
** The "S" for heats 20 and 21 have not been included in this calculation because of the absence of silicon analysis.

TABLE 7—Composition of 26 Heats of Type 316

Heat No.	% C	% Cr	% Ni	% Mo	% Mn	% Si
1	0.042	17.73	12.95	2.18	1.96	0.72
2	0.045	17.98	12.85	2.19	1.93	0.57
3	0.050	17.59	12.76	2.14	1.86	0.63
4	0.028	17.51	13.82	2.45	1.91	0.54
5	0.055	17.45	13.50	2.01	1.96	.....
6	0.041	17.38	13.53	2.22	1.92	0.48
7	0.053	17.36	12.68	1.89	1.69	0.44
8	0.019	17.12	13.36	2.65	1.06	0.28
9	0.022	17.33	12.91	2.28	0.90	0.36
10	0.020	16.16	13.22	2.20	1.60	0.47
11	0.018	18.54	12.84	3.00	0.71	0.27
12	0.019	18.56	12.64	2.85	1.06	0.38
13	0.022	18.45	12.69	3.03	1.25	0.31
14	0.050	18.07	12.68	2.38	1.78	0.36
15	0.060	17.78	12.79	2.20	1.74	0.53
16	0.025	18.54	13.76	2.75	1.39	0.46
17	0.030	18.05	10.54	2.30	1.42	0.35
18	0.046	17.70	13.00	2.15	2.00	0.59
19	0.041	17.55	13.35	2.42	1.66	0.50
20	0.043	17.86	13.08	2.20	1.79	0.51
21	0.025	19.49	12.56	2.24	0.74	0.30
22	0.040	17.73	13.16	2.37	1.83	0.31
23	0.053	17.44	13.20	2.28	1.42	0.42
24	0.046	17.39	12.70	2.42	1.68	0.61
25	0.024	16.84	10.42	2.55	0.90	0.36
26	0.026	17.60	12.65	2.00	1.60	0.54

2. Nitrogen content (not ordinarily reported).
3. Analytical errors.
4. Improper test procedures.
5. Variations in austenite balance.
6. Incomplete sensitization.
7. Cold work.
8. Grain size.
9. Grain fall-out.

Because the curves show relatively poor correlation, indicating that factors other than composition predominate in determining corrosion rates in the Huey Test, it was concluded that special compositional requirements were not justified from a practical standpoint.

Current procedure is to purchase commercial Type 347 to ASTM specifications, requiring that it demonstrate resistance to intergranular corrosion in qualification tests. It is concluded that variations in composition within the nominal limits will not significantly affect the overall corrosion resistance. The assumption is made that the 18-8 chromium-nickel-columbium composition has been properly selected for the specific application involved and that only intergranular corrosion resistance will be considered.

Chromium-Nickel-Molybdenum Grades

The situation in regard to the chromium-nickel-molybdenum steels is somewhat

more complicated. Inherent difficulties lie in the selection of an appropriate qualification test[9,10,11] and in a divergence of opinion concerning the required level for certain elemental components.

The problems associated with the use of the Huey Test have been widely discussed. The use of the ferric sulfate or nitric-hydrofluoric acid tests, possibly in conjunction with the oxalic acid screening test, probably will resolve satisfactorily the question of determining susceptibility to intergranular corrosion. Whether or not the carbide-precipitated or sigma-phase areas which are attacked in the several qualification tests will actually be a factor in plant processes must be determined by empirical tests.

There remains, however, the fact that there is a tendency to use qualification tests—particularly the Huey Test—as an indication of overall or general corrosion resistance.

Actually, it is difficult even for annealed chromium-nickel-molybdenum stainless steels to pass the Huey Test. This is because the element added to increase resistance to reducing media (i.e., molybdenum) diminishes the resistance of the alloy to nitric acid.[12] Although this has been recognized for some time, the specific effect in other media has not been investigated except in a general way nor, to the author's knowledge, has the influence of the other components been investigated when combined in this particular type of alloy.

Because of the interest in a realistic appraisal of compositional effects in these grades, an investigation was made both of response in standard qualification tests and of behavior in plant processes.

The behavior of 24 heats of Type 316 in the Huey test, randomly selected, was analyzed by the method previously described. The compositional data are given in Table 5. Corrosion rates obtained for these compositions are shown in the last column of Table 6. The curves derived are shown in Figure 3, including data from four special compositions tested at the Texas City plant. (It will be observed that the general indications from an analysis of the four Texas City heats show the same tendency as those from the more detailed analysis of the 24 heats tested by Metals Research).

The highly beneficial results of increased chromium content are readily apparent, as is the adverse effect of molybdenum discussed above.

More striking, however, are the adverse effects of silicon (see Figure 1) and of nickel. The former is worthy of note for reasons previously discussed, while the latter effect may be the basis for certain apparently unsupported feelings in the chemical industry against high nickel contents.

The verification data of the curves is given in Table 6 and Figure 4. The data indicate that the curves are quite satisfactory in explaining the observed behavior. The correlation is much better than for Type 347 (Figure 2).

A similar analysis was made of 26 heats reported by Warren[10] in the proposed nitric-hydrofluoric acid test. The composition of the heats (selected for the widest possible compositional spread) and their corrosion rates in the nitric-hydrofluoric acid test are given in Tables 7 and 8. The curves derived from the data are given in Figure 5. Verification data are given in Table 8 and Figure 6.

It will be immediately observed that in this instance *all alloying elements are beneficial.* It would be expected then that the more highly alloyed heats would be the most resistant, and an examination of Warren's data will indicate that this is so. Such a statement can by no means be made in regard to the data previously considered from the Huey Test.

An interesting observation is that all of the 80 heats originally tested by Warren gave rates of less than 0.0010 IPM in the Huey Test, although the overall compositional range was:

Chromium	16.16 to 19.49%
Nickel	10.42 to 13.82%
Molybdenum	1.89 to 3.03%
Carbon	0.017 to 0.060%
Manganese	0.71 to 2.16%
Silicon	0.15 to 0.88%

This suggests that, in balanced compositions, adverse and beneficial elements tend to counteract each other.

It is apparent, then, that the alloying elements may have quite different effects in varying environments. A logical result of this observation is (1) the inquiry as to what results can be found in specific chemical processes, and (2) whether there is a *significant* difference in behavior when the composition is varied, for better or worse, between the established commercial limits.

In an effort to answer these questions, at least in part, a field test program was initiated on four different heats procured from the Carpenter Steel Company. At a later date, three more heats were procured for more extensive tests. The composition of the experimental heats are given in Table 9.

The results of the field corrosion tests (Table 10) on the first four heats indi-

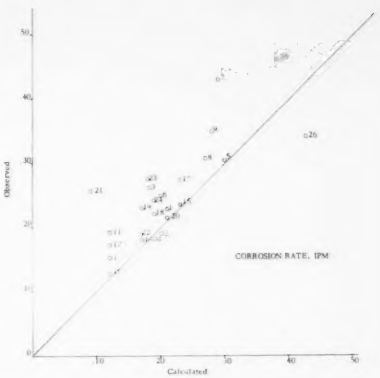

Figure 6—Graphical correlation of calculated vs observed corrosion rates for Type 316 stainless steel in nitric-hydrofluoric acid test.

TABLE 8—Verification of Curves for Type 316 in Nitric-Hydrofluoric Acid

Heat No.	f (Cr)	f (Ni)	f (Mo)	F (Mn)	F (Si)	S	f′ o*	fo
1	0.26	0.315	0.325	0.235	0.28	1.415	0.217	0.23
2	0.24	0.32	0.325	0.235	0.28	1.400	0.202	0.19
3	0.275	0.32	0.34	0.245	0.28	1.460	0.262	0.18
4	0.29	0.30	0.27	0.24	0.28	1.380	—0.182	0.19
5	0.295	0.305	0.39	0.235	0.28	1.505	0.307	0.30
6	0.305	0.305	0.315	0.24	0.28	1.445	0.247	0.20
7	0.31	0.32	0.45	0.27	0.28	1.630	0.432	0.29
8	0.35	0.305	0.25	0.32	0.28	1.505	0.307	0.27
9	0.315	0.32	0.30	0.335	0.28	1.550	0.352	0.28
10	0.64	0.31	0.32	0.27	0.28	1.820	0.622	0.54
11	0.21	0.32	0.235	0.35	0.28	1.395	0.197	0.12
12	0.21	0.325	0.24	0.32	0.28	1.375	0.177	0.12
13	0.215	0.325	0.235	0.30	0.28	1.355	0.157	0.12
14	0.235	0.325	0.29	0.25	0.28	1.380	0.182	0.17
15	0.26	0.32	0.32	0.255	0.28	1.435	0.237	0.23
16	0.21	0.30	0.245	0.29	0.28	1.325	0.127	0.12
17	0.235	0.37	0.30	0.29	0.28	1.475	0.277	0.23
18	0.265	0.315	0.33	0.23	0.28	1.420	0.222	0.19
19	0.28	0.32	0.28	0.265	0.28	1.425	0.227	0.17
20	0.25	0.315	0.32	0.25	0.28	1.415	0.217	0.21
21	0.18	0.325	0.32	0.35	0.28	1.455	0.257	0.09
22	0.26	0.31	0.29	0.25	0.28	1.390	0.192	0.17
23	0.30	0.31	0.30	0.285	0.28	1.475	0.277	0.18
24	0.30	0.32	0.28	0.26	0.28	1.440	0.242	0.19
25	0.415	0.37	0.26	0.335	0.28	1.660	0.462	0.36
26	0.28	0.32	0.39	0.27	0.28	1.540	0.342	0.43
Total** 36.860								5.77
Average 1.418								0.22
								—1.418
								a—1.198

*f′o = S + a where a = fo (Avg.) — S (Avg.)
**The "S" for heats 20 and 21 have not been included in this calculation because of the absence of silicon analysis.

TABLE 9—Composition of Experimental Heats of Chromium-Nickel-Molybdenum Steels

Heat No.	Cr	Ni	Mo	Mn	Si	C
1	17.1	12.6	2.5	1.75	0.66	0.05
2*	18.4	10.2	2.7	1.52	0.62	0.07
3	16.5	10.5	2.4	1.76	0.75	0.10
4	17.7	13.5	2.2	1.73	0.43	0.02
5	20.5	14.5	2.9	1.66	0.52	0.06
6	18.7	14.2	2.9	1.47	0.43	0.08
7	16.4	10.9	1.9	1.92	0.70	0.08

Range of composition embraced:

Chromium	16.4 —20.5
Nickel	10.2 —14.5
Molybdenum	1.9 — 2.9
Manganese	1.47— 1.92
Silicon	0.43— 0.75
Carbon	0.02— 0.10

* Estimated 8 percent ferrite.

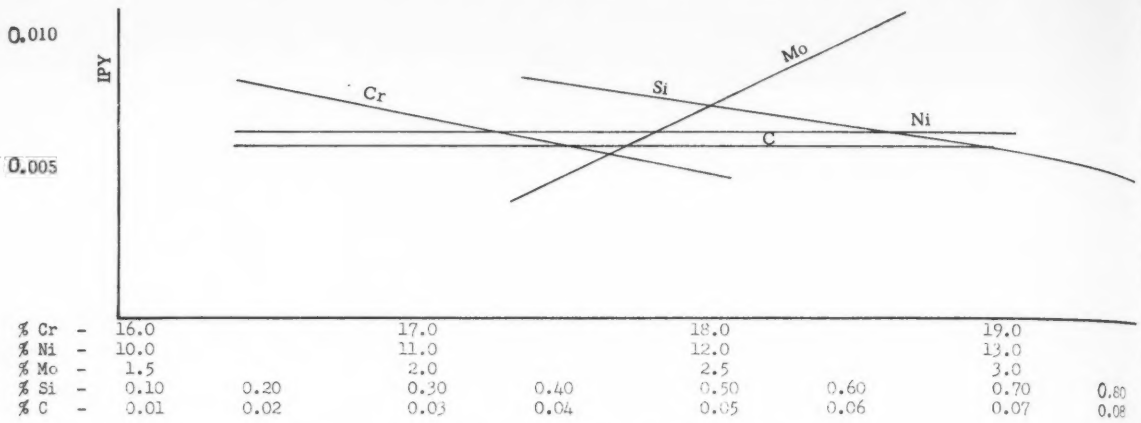

Figure 7—Composition of Type 316 vs corrosion rates in acetic acid recovery system.

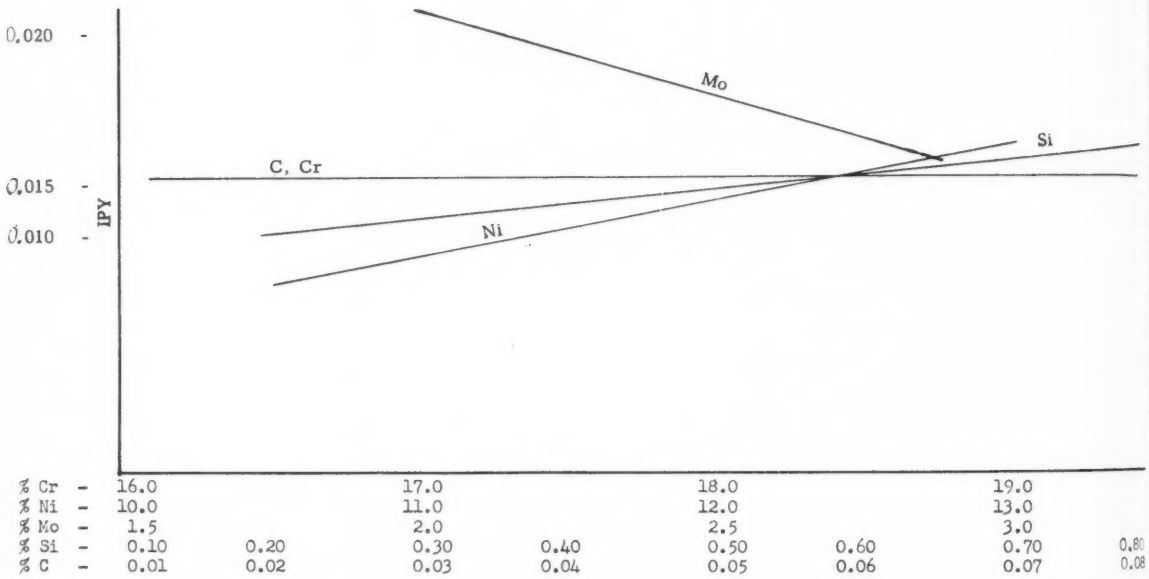

Figure 8—Composition of Type 316 stainless steel vs corrosion rates in acetic acid esterification process.

cate either that the beneficial and detrimental constituents virtually balance the effect of each other or that operational variables greatly override the effects of the variations in composition. Possibly both conditions exist.

Of the 31 exposures, there was no practical difference in the corrosion rates of heats 1 through 4 (i.e., all rates ± 0.001 IPY) in 20 instances. In only one case (10b) was the expected order of resistance (heats 2, 4, 1, 3) observed, although two more cases (4f and 5a) showed reasonably predictable behavior. The remaining eight cases varied most unpredictably. The apparently predictable sequences were not repeated in successive tests in the same nominal environments.

Figures 7-10—derived from graphical analyses of heats 1 to 4 in several field tests—indicate the wide variation in influence of individual alloying elements in different process streams. Since the exposures were made in processes in which Type 304 is definitely unsatisfactory and the molybdenum-bearing grades are required, the curves for molybdenum are of particular interest. Figures 7 and 9 then indicate that the maximum beneficial effect from molybdenum in those environments is obtained in the vicinity of 2 percent (since 304 is not satisfactory, the curves must be part of a parabola), with a detrimental effect at higher concentrations. Figures 8 and 10, on the other hand, represent environments in which molybdenum contents higher than those in commercial 316 might be beneficial. As previously indicated, however, the practical effects of the variations are insignificant.

A wider field test program has been conducted on the heats 5, 6 and 7—representing more or less extreme ranges in the chromium-nickel-molybdenum steels. The data are given in Table 11.

In these 26 exposures, no significant difference was observed in 21 of the cases. None of the exposures showed the expected order of resistance (heats 5, 6, 7). In four cases (Nos. 6, 7a, 8 and 15b), the very low chromium Type 316 (heat 7) is the least resistant but significantly so only in the two latter instances. In one instance, this heat is significantly better than a nominal 317 analysis.

Summarizing all tests, then, it will be observed that there is usually no practical difference in the corrosion rate of the four heats in Table 10 and the three in Table 11 in the process environments in which they were field tested.

In the few cases in which differences are observed, the differences are erratic, not readily attributable to composition, and in general quite unpredictable.

Conclusions

The Huey Test data for Type 347 suggested that an improvement might be

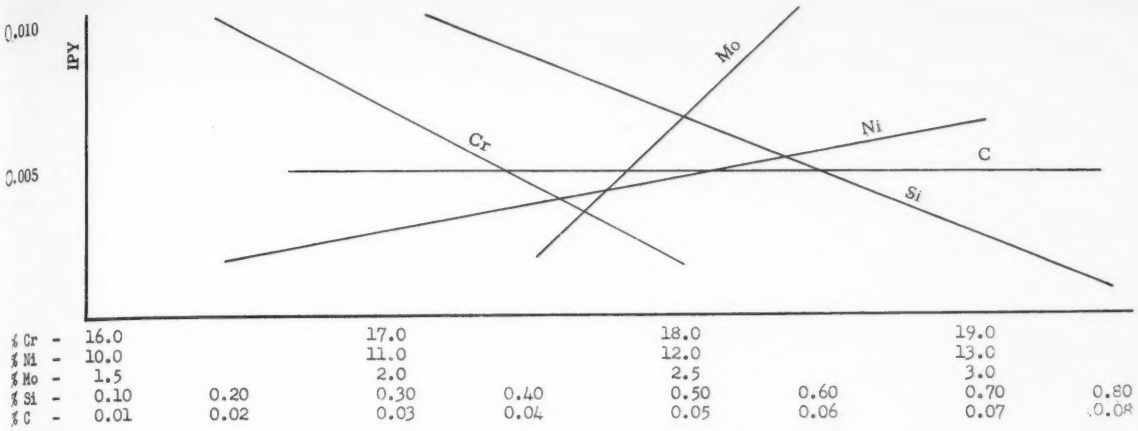

Figure 9—Composition of Type 316 stainless steel vs corrosion rates in amine refining system.

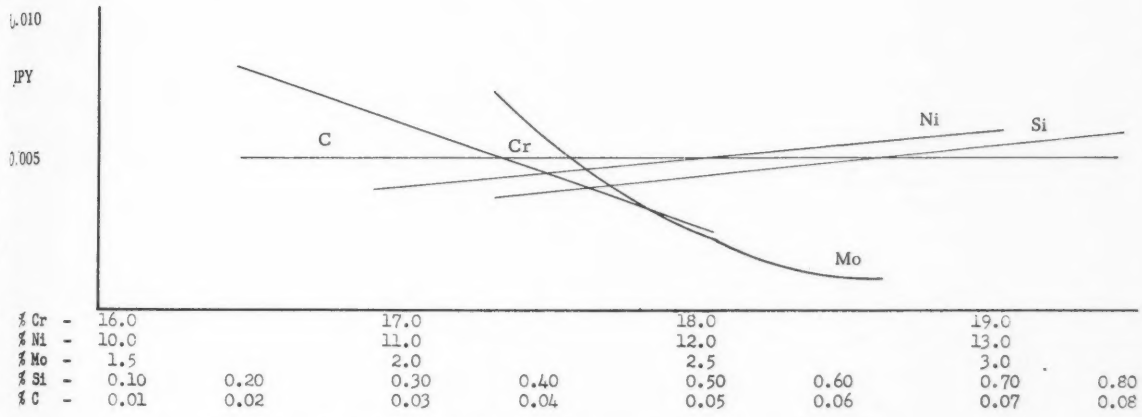

Figure 10—Composition of Type 316 stainless steel vs corrosion rates in crude amine stripping system.

effected by more rigorous control of silicon content, but that the qualification tests are probably adequate proof against substandard material.

The data for the chromium-nickel-molybdenum grades of stainless steel indicate a negligible difference, practically speaking, between alloys within the commercial analysis range.

Chromium in the Type 316 alloys is unquestionably beneficial provided that the austenite balance is unaffected and that the benefits are not offset by the concentration of some element(s) having a deleterious effect. The chromium content in the commercial range appears to be adequate, although the high side may be preferred from the standpoint of insurance against unforeseen attack.

Acknowledgments

The author gratefully acknowledges the assistance and cooperation of L. S. VanDelinder and R. L. Davisson of the Materials of Construction Group, Development Department, Union Carbide Chemicals Company, and of W. G. Ashbaugh of the Corrosion Group, Texas City Plant, in assembling and interpreting the data. Thanks also are extended to the Carpenter Steel Company for providing the experimental heats of chromium-nickel-molybdenum stainless steel. Portions of the data have been separately presented to the Materials Engineering Committee of the Union Carbide Corporation Engineering Liaison Program.

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DISCUSSION

Question by Karl E. Luger, Houston, Texas:

Were the chromium-nickel-molybdenum samples which were tested in the Huey solution sensitized or were they quench annealed?

Reply by C. P. Dillon:

All of the results tabulated for the Type 316 samples were derived from the data of Warren (Table 6 of reference 10 in the report) using annealed specimens of the 316 analysis. Mr. Warren obtained the test heats from various steel producers. These were tested by him in the "commercially annealed" condition only after the electrolytic oxalic acid etch test and a Huey test revealed "that there was no evidence of either precipitated carbides or prior plastic deformation."

TABLE 10—Corrosion Tests on Four Experimental Heats of Chromium-Nickel-Molybdenum Stainless Steel*

Test No.	Conditions	HEAT NUMBER 1	2	3	4
1	Huey Test, 3—48 hour periods	0.020	0.017	0.022	0.012
2	504 hours in crude acetic anhydride distillation	0.001	0.001	0.002	0.001
3	100 hours in butyl acetate esterification	0.019	0.014	0.017	0.018
4	a. 432 hours in crude acetic acid distillation	0.007	0.002	0.005	0.006
	b. 550 hours in crude acetic acid distillation	0.001	0.001	0.001	0.001
	c. 1296 hours in crude acetic acid distillation	0.001	0.001	0.004	0.003
	d. 168 hours in crude acetic acid distillation	0.002	0.000	0.001	0.006
	e. 360 hours in crude acetic acid distillation	0.002	0.000	0.001	0.000
	f. 1776 hours in crude acetic acid distillation	0.002	0.001	0.008	0.003
5	a. 720 hours in crude ethylenamines distillation	0.005	0.000	0.006	0.005
	b. 816 hours in crude ethylenamines distillation	0.001	0.002	0.002	0.001
	c. 1440 hours in crude ethylenamines distillation	0.001	0.001	0.001	0.001
	d. 2424 hours in crude ethylenamines distillation	0.001	0.000	0.000	0.000
6	a. 720 hours in acetic acid distillation residue	0.009	0.007	0.006	0.006
	b. 770 hours in acetic acid distillation residue	0.008	0.007	0.006	0.005
	c. 1055 hours in acetic acid distillation residue	0.014	0.012	0.013	0.012
	d. 3240 hours in acetic acid distillation residue	0.011	0.011	0.011	0.010
7	a. 815 hours in refined amines distillation	0.001	0.000	0.000	0.001
	b. 744 hours in refined amines distillation	0.001	0.000	0.000	0.000
	c. 672 hours in refined amines distillation	0.005	0.002	0.001	0.001
	d. 456 hours in refined amines distillation	0.002	0.001	0.001	0.002
	e. 2372 hours in refined amines distillation	0.001	0.001	0.001	0.001
8	a. 984 hours in refined acetic anhydride distillation	0.000	0.000	0.000	0.000
	b. 770 hours in refined acetic anhydride distillation	0.000	0.000	0.000	0.000
9	a. 1056 hours in crude hydroxy amine distillation	0.000	0.000	0.000	0.000
	b. 4300 hours in crude hydroxy amine distillation	0.000	0.000	0.000	0.000
10	a. 432 hours in crude caustic: HCl mixture	0.004	0.003	0.003	0.004
	b. 1850 hours in crude caustic: HCl mixture	0.035	0.027	0.039	0.030
11	a. 720 hours in crude acetate ester distillation	0.003	0.003	0.003	0.003
	b. 600 hours in crude acetate ester distillation	0.002	0.002	0.002	0.002
	c. 3240 hours in crude acetate ester distillation	0.002	0.001	0.002	0.002

* In IPY.

TABLE 11—Corrosion Tests of Three Experimental Heats of Chromium-Nickel-Molybdenum Stainless Steel*

Test No.	Conditions	HEAT NUMBER 5	6	7
1	Huey Test, 5—48 hour exposures	0.009	0.011	0.010
2	1350 hours in steam-stripped chlorinated solvent	0.001	0.002	0.002
3	1100 hours in distillation of aqueous amines	0.001	0.001	0.001
4	a. 1100 hours in flash separation of aqueous amines	0.001	0.001	0.002
	b. 400 hours in flash separation of aqueous amines	<0.001	<0.001	<0.001
5	500 hours in crude amine distillation	0.002	0.002	0.003
6	3200 hours in refined amine distillation	0.002	0.002	0.004
7	a. 1000 hours in crude acetic acid distillation	0.001	0.001	0.003
	b. 2500 hours in crude acetic acid distillation	<0.001	<0.001	<0.001
8	1100 hours in dilute solution acrylic acid in solvents	0.037	0.027	0.165
9	2500 hours in stripping of crude pyridine derivatives	0.000	0.001	0.002
10	3400 hours in stripping esters from 95% acetic — 5% butyric acid	0.002	0.002	0.002
11	260 hours in stripping acrolein from dilute organic acids	<0.001	<0.001	<0.001
12	662 hours in propionic acid refining			
	a. Base of column	<0.001	<0.001	<0.001
	b. Middle of column	<0.001	<0.001	<0.001
	c. Feed line	<0.001	<0.001	<0.001
	d. Top of column	<0.001	<0.001	<0.001
13	120 hours in oxidation reaction system			
	a. Reactor	<0.001	<0.001	<0.001
	b. Decanter	<0.001	<0.001	<0.001
14	984 hours in toluene solution of chlorinated aromatic esters			
	a. Primary reactor	0.062	0.062	0.064
	b. Primary reactor vapor line	0.005	0.005	0.005
	c. Secondary reactor	0.002	0.002	0.002
15	3450 hours in chlorine reaction with polymer			
	a. Liquid	0.002	0.002	0.002
	b. Vapor	0.037	0.029	0.050
16	255 hours in crude toluene containing chlorides			
	a. Kettle	0.027	0.020	0.022
	b. Column Base	0.005	0.005	0.005

* In IPY.

Question by Fred W. S. Jones, Rosemere, Quebec, Canada:

Would you please comment on the advantages which may be obtained in the use of Type 319 specification, as an alternate to Type 316 stainless steel?

Reply by C. P. Dillon:

The Type D319 analysis could and should be used where proprietary analyses of the molybdenum bearing stainless steels are currently specified. However, the corrosion engineer should establish factually that the special analysis is required for a given environment before specifying an analysis other than the available Type 316.

Comments by John Manning, Celanese Corp., Charlotte, N. C.:

A program similar to the one you describe was initiated several years ago by Celanese on compositional effects within the 316 stainless steel range on corrosion rates in acetic acid environments. The results confirm your findings that in most cases no significant differences in rates were noted. However, exceptions to this were noted in acetic acid solutions where sulfuric acid type constituents were present and where strongly oxidizing environments were encountered. In our experience, the multiple curvilinear regression method of statistical analysis was found most suitable to this type of study.

Reply by C. P. Dillon:

Your substantiation of this study is appreciated. Any but the most simple of exposures presents a new corrosion problem. Complex mixtures of corrosive chemicals in a plant process stream pose a problem in providing the optimum economic alloy specification. However, available commercial alloy compositions cover such a broad range that a material can be found to resist the environment without resorting to the use of a special analysis.

Your comments regarding acetic acid solutions are interesting. We have also observed the exceptions noted by you. In one instance, a Type 304 analysis was superior to the Type 316 in an acetic acid solution under strongly oxidizing conditions. The tables in the report indirectly report a comparison of acetic acid with and without sulfuric acid added. The effect of molybdenum in improving the corrosion rate was particularly noticeable in the medium containing sulfuric acid.

Any discussion of this article not published above will appear in December, 1960 issue.

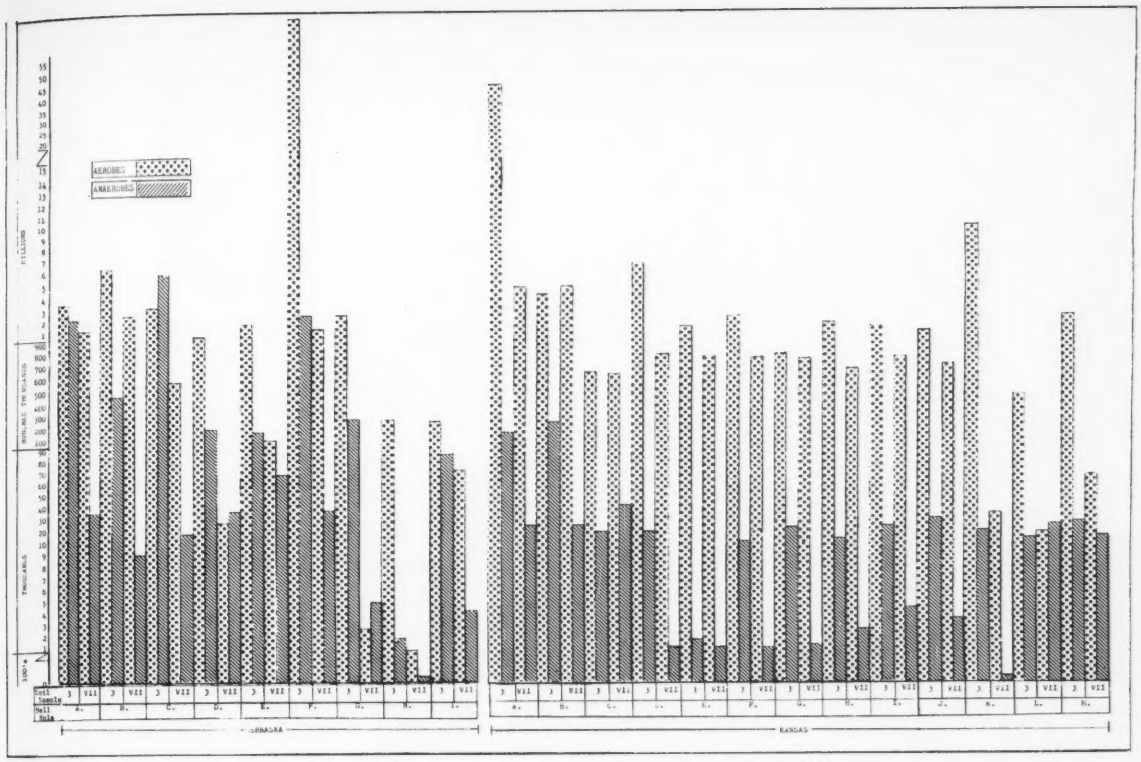
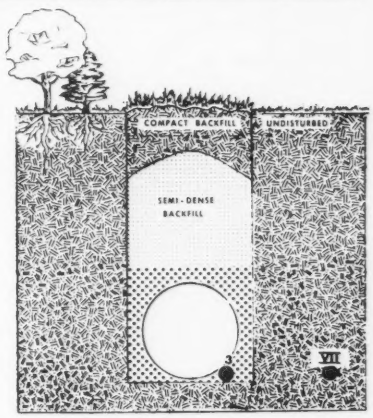


Figure 1—Soil bacteria per gram of soil Sample 3—ditch bottom located next to the pipe. Sample VII—same depth but 12 feet to 15 feet away from pipe line in undisturbed soil of the right-of-way. (See location of samples on diagram below.) Samples were from Nebraska and Kansas.



Soil Microorganisms in Relation to Cathodically Protected Pipe*

By J. O. HARRIS

Introduction

MICROBIAL ACTIVITIES which are related to cathodic protection fall into two general classes depending on whether a coated pipe or bare metal is in contact with the soil. Obviously if a perfect coating situation existed, cathodic protection would not be needed. Hence the main relationship of bacteria to a coated system has to do with the action of microorganisms in the deterioration or loss of electrical insulation values or destruction of the coating systems.

A research project at Kansas State University has been concerned with this phase of the problem. Previous observations have been published.[1,2] An extension of these observations and review of the project to the current time will comprise the first portion of this discussion.

A great deal of attention has been given to the action of the anaerobic sulfate-reducing bacteria with respect to the action of soil microorganisms on bare metals. Data obtained from an extensive study of the environment in back-filled pipe line ditches indicate that aerobic conditions are common in soil adjacent to buried pipe lines. Some of the ways in which this presence of oxygen and the resulting bacterial development could contribute to corrosion of bare metals will be discussed in relation to the electrochemical activities of living cells.

Microbial Deterioration of Pipe Line Protective Coatings

Field samples from 14 states taken along operating oil and gas pipe lines show that the pipe line ditch represents a definite man-made disturbance of the natural biological and physical equilibrium conditions within the soil. Harris[2] found conditions in soil adjacent to the coatings on pipe surfaces that were favorable for microbial development, regardless of the depth, the temperature of the line, the moisture, or the acid-alkaline reaction of the soil. Comparisons

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Abstract

Tests were made to determine whether soil microorganisms could alter the insulating value of coatings intended for use on cathodically protected buried pipe. The microbial corrosion of bare metal also is considered.

Data tabulated from more than 150 bellholes show that a pipe line ditch represents a definite alteration of natural undisturbed soil equilibrium conditions. Moisture was found to be present in greater amounts in the bottom of pipe line ditches than in undisturbed soil. The presence of aerobic conditions and the high bacterial populations adjacent to coated pipe lines suggest the importance of microbial decomposition of coating materials. An experimental setup with data was presented to show electrical potentials developed by common soil bacteria in contact with bare steel and carrying on normal metabolism.

Data reported include soil bacteria count per gram of soil, percent soil moisture at ditch bottoms adjacent to pipe lines, comparison of moisture present at soil surfaces and equivalent pipe line depths, and moisture in coatings samples removed from pipe after years of underground service. The significance of these data in relation to cathodic protection is considered. 3.3.4

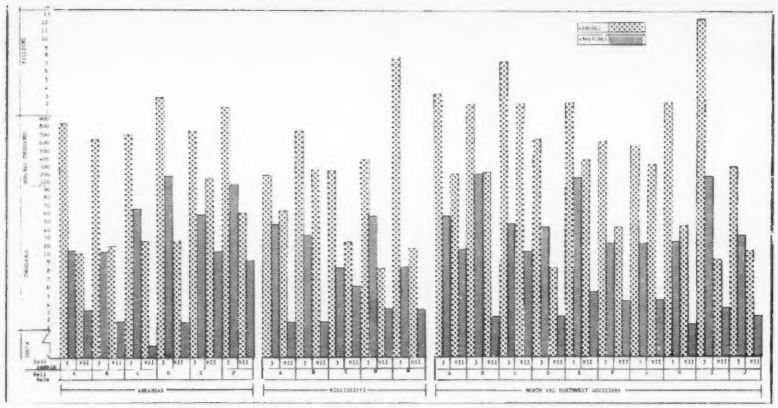

Figure 2—Soil bacteria per gram of soil (Arkansas, Mississippi, and north and northwest Louisiana).

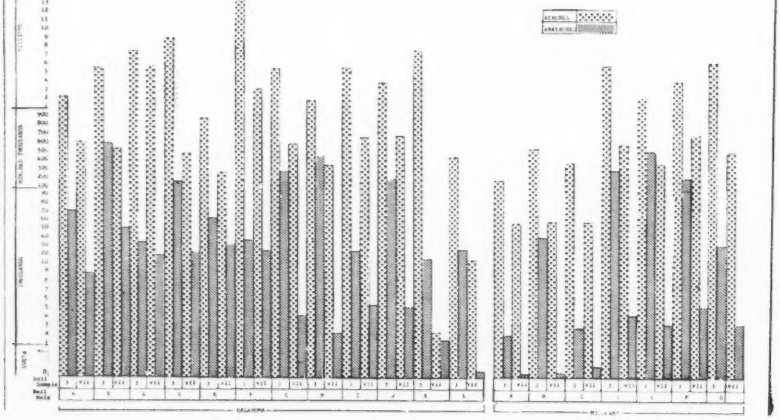

Figure 3—Soil bacteria per gram of soil (Oklahoma and Missouri).

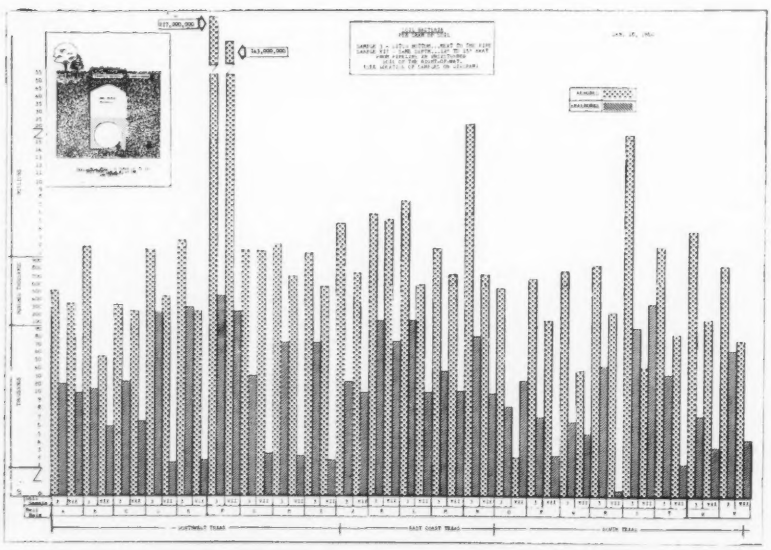

Figure 4—Soil bacteria per gram of soil (Southwest Texas, East Coast Texas, South Texas).

About the Author

JOHN O. HARRIS has been on staff of Kansas State University since 1941. He is professor of bacteriology and bacterial physiologist at the Kansas Agricultural Experiment Station. An NACE member, he has a BS and PhD from Kansas State and an MS from the University of Hawaii. His research work has included hydrocarbon oxidation, asphalt road deterioration and pipe line coating breakdown.

of the numbers of bacteria found adjacent to coated lines with numbers found at the same depth but in undisturbed soil of the right-of-way indicated that the soil bacteria were obtaining food material from the coating or wrapping materials.

A summary of 230 soil samples (of more than 800) from representative locations as shown in Figures 1-5 illustrates these comparisons. The high counts of bacteria which grow under aerobic conditions (presence of O_2) when compared with anaerobic types (absence of O_2) indicates oxygen diffusion to pipe line depths.

Isolation of pure cultures of the bacteria found revealed no startling results as to the kinds of microorganisms present. Bacteria commonly present in most soils were those constituting the predominant population. Of interest however were the large numbers of bacteria which could grow on hydrocarbon materials as their sole source of energy. These forms have been found in all the soil samples at bell-holes examined at both the surface and next to the pipe at ditch bottom.

Many bacteria have been isolated from the moisture found under unbonded asphalt or tape coatings. All types reported earlier[1] have been encountered many times, and growth patterns are similar to those described. Asphaltic and wax type coatings, the adhesive or bonding agents of plastic tapes, and certain of the plastics themselves served as readily available food materials. Coal tar type coatings, however, did not show utilization by the bacteria.

Typical forms of these bacteria are shown in Figures 6 to 9 inclusive.

Figure 6 is an electron microscope picture of *Micrococcus paraffinae*, one of the spherical shaped forms often isolated.

Figure 7 represents the same type of bacteria upon which a very thin film of gold has been deposited thus giving a "shadowed" effect indicating the actual shape of the cells.

Figure 8 pictures Pleomorphic rods shadowed with gold to show their cylin-

drical form. Also apparent are a few flagella which allow these types to move through the soil.

Figure 9 shows a culture of *Pseudomonas aeruginosa*. These forms are highly resistant to radiation and are not susceptible to many common antibiotics.

These bacteria are not the anaerobic sulfate reducers but represent bacteria widely distributed in nature and commonly found in all the bell-holes sampled. They comprise the same group as were found in high populations at the soil-asphalt interface of highways.[3]

Soil and Coating Moisture Studies

The field sampling data showed that soil in the bottom of the back-filled pipe line ditch was a zone of high moisture content as compared with undisturbed soil at comparable depths. A tabulation of moisture present in 115 soil samples from representative locations at ditch bottom, together with soil types is shown in Figure 10. Free water was present in the ditch bottom at a number of the locations.

It should be recognized that the surface of the soil gives a very poor indication of the water present at pipe line depths even in an undisturbed normal soil situation as in the right-of-way some distance from the ditch. Soil moisture data collected by the U. S. Weather Bureau Stations at four different locations in the United States is shown in Figure 11. The charts show surface moisture as compared to the moisture content at pipe line depths. Since these data were collected to be related to crop production, the water content has been expressed in inches available moisture. For example, a value of 2.4 at one level indicates that the water is equivalent to a 2.4 inch rainfall. From these charts a number of examples can be seen in which the surface of the soil was dry while considerable water was present at the four foot level. These summaries of normal soil conditions serve to further the conclusion that the pipe line ditch represents an unnatural condition with respect to soil moisture.

The water in contact with coating materials in the soil bears a definite relationship to the water content of the coatings which have the property of absorbing water. Data published earlier[2] with respect to moisture content of field samples of coating is believed to represent the first confirmation (using field samples) of various laboratory tests carried out by a number of producers and consumer laboratories.

Figures 12 and 13 summarize additional data gathered which agree with the earlier reports. Coal tar coatings absorb little water while the moisture content of asphalt varied with the length of time the coating had been in contact with the soil and the water content of the soil. The condition of the pipe surface was recorded when samples were removed.

Thus the environment of the back-filled pipe line ditch forms a favorable situation for microbial development. The semi-dense, non-compacted zone of the back-fill above the pipe allows for better aeration of the soil. The adequate moisture coupled with the actual high bacterial counts represent indications that microbial attack may represent an important factor in coating deterioration or loss of electrical insulation.

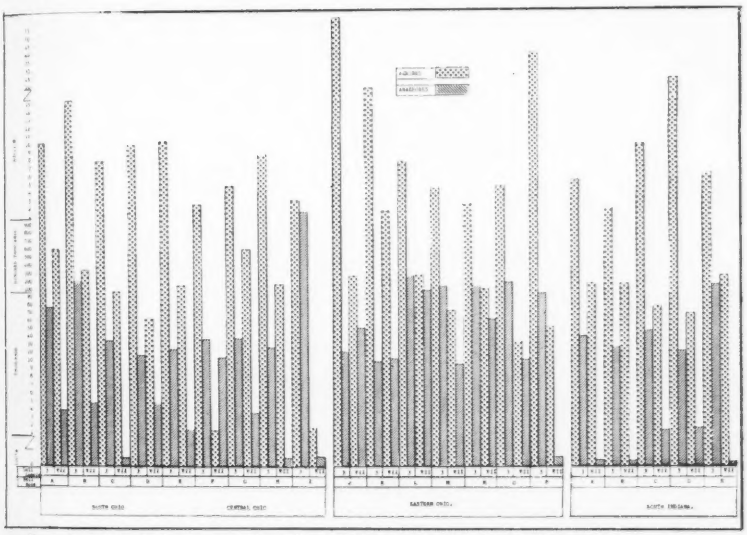

Figure 5—Soil bacteria per gram of soil (South Ohio, Central Ohio, Eastern Ohio and South Indiana).

Research Work in Progress

Current research on the project at Kansas State University is aimed at extending the field studies over a wider

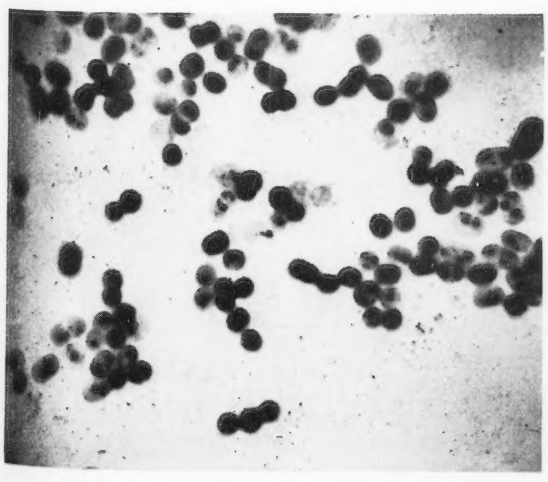

Figure 6—*Micrococcus paraffinae* photographed to bring out cell structure—different ages—granules (black dots) which form a part of their ability to digest or use carbon sources as a source of energy. Approximately 6000X.

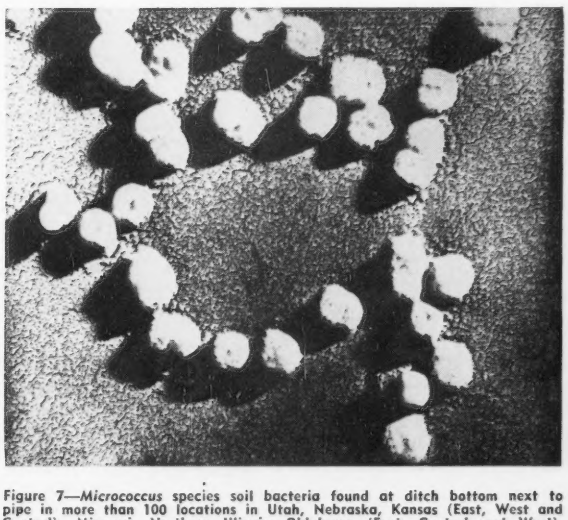

Figure 7—*Micrococcus* species soil bacteria found at ditch bottom next to pipe in more than 100 locations in Utah, Nebraska, Kansas (East, West and Central), Missouri, Northern Illinois, Oklahoma (East, Central and West), Texas (Southwest, Gulf Coast and South), Louisiana (North and Central), Arkansas, Mississippi, Southern Indiana, Ohio (Central and Southern), West Pennsylvania and Northwest Virginia. Approximately 8500X. This electron microscope photograph was made to show the three-dimensional shape of this species by shadow-casting with gold.

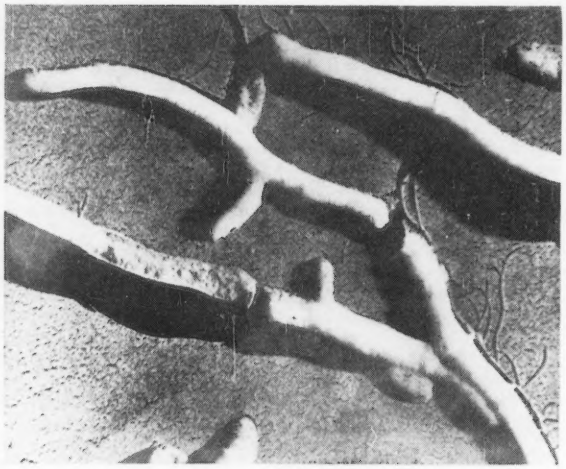

Figure 8—Pleomorphic rod species, a distinct type of the many rod-shaped bacteria found in soil next to the pipe at ditch bottom. This electron microscope photograph was made to show the flagella along the cells (their means of locomotion) and also to show the three-dimensional shape of this species by shadow-casting with gold. Approximately 9500X.

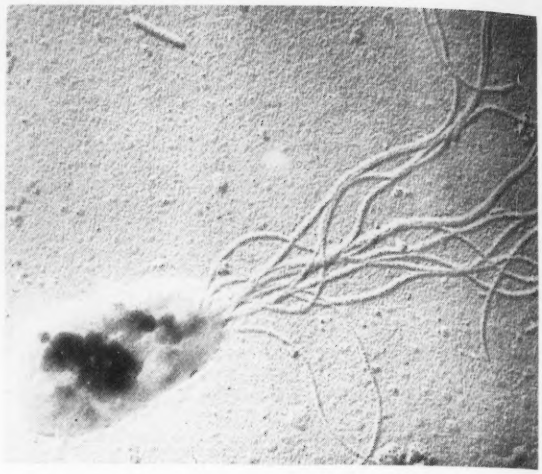

Figure 9—Typical rod-shaped bacteria such as *Pseudomonas* and *Flavobacterium* types—photographed by shadow-casting with a thin film of chromium condensed on the surface to show fine structure and the long thread-like flagella by which these bacteria are able to move about. Approximately 16,500X.

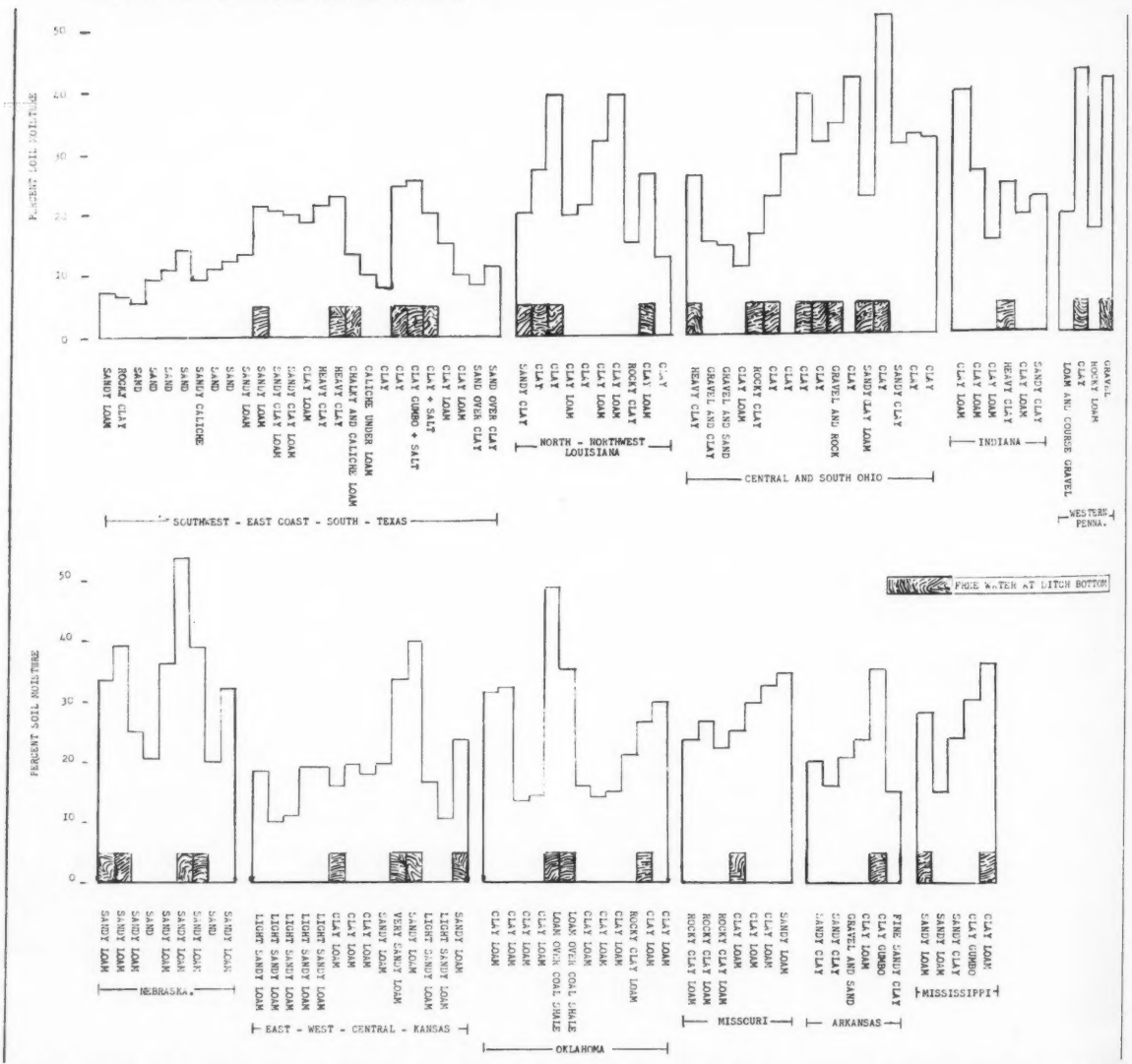

Figure 10—Percent soil moisture at ditch bottom immediately adjacent to pipe lines. The 115 bell-holes at 17 locations represent average pipe line ditch.

geographical area covering various soil and climatic conditions.

A number of bell-hole samplings have been planned in areas ranging from southern Texas to the Canadian oil fields and from the West Coast to the Atlantic Seaboard. The mobile field laboratory pictured in Figure 14 was equipped to facilitate field inspections and to make duplicate analyses thus allowing a control of any possible effects of shipping samples. All soil and coating samples were then sent to the Department of Bacteriology laboratories at Kansas State University for complete analyses. Figure 15 shows glassware used in making analyses on samples from a single bell hole.

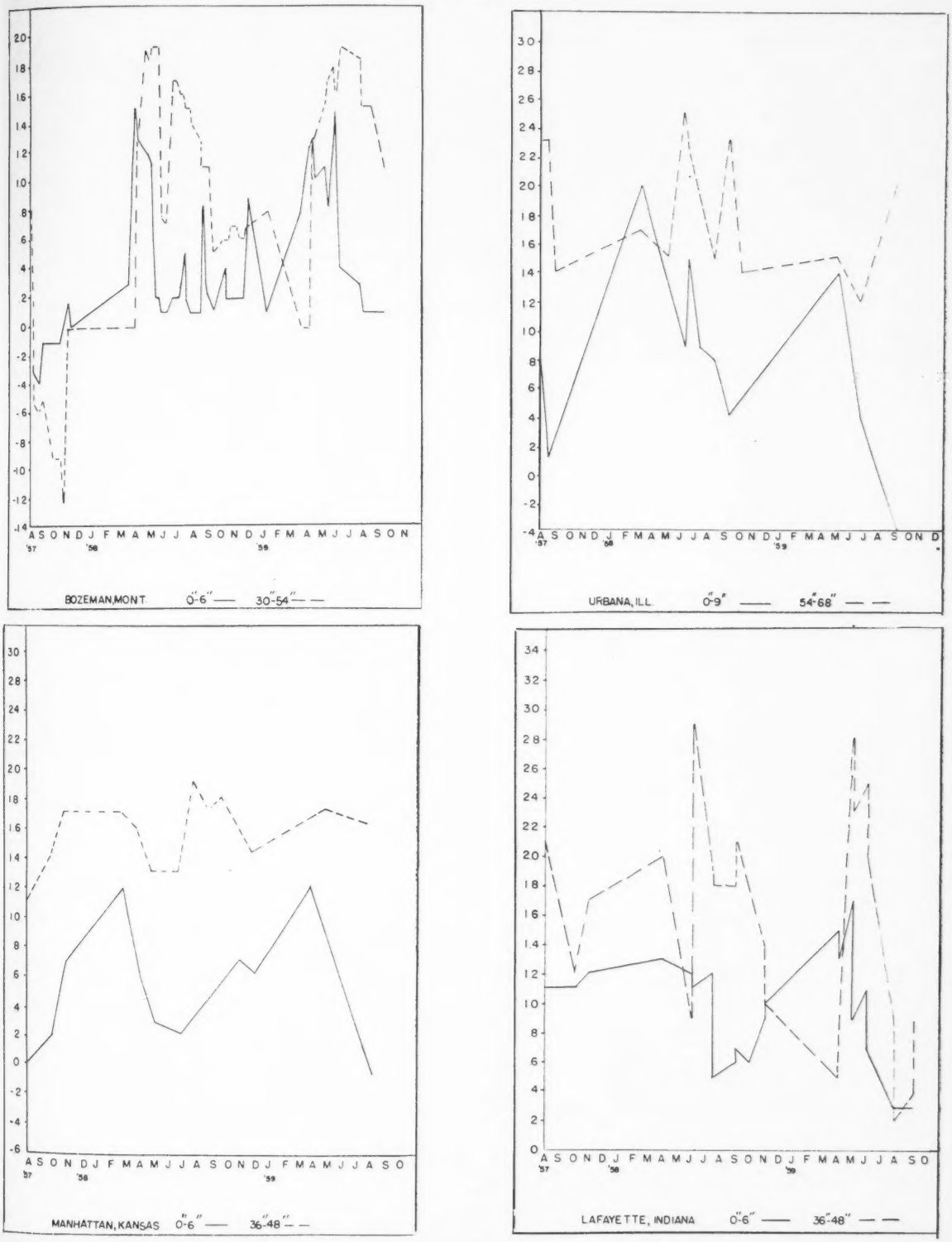

Figure 11—A comparison of moisture present at soil surfaces and equivalent pipeline depths for soil moisture at four United States Weather Bureau stations.

Once it was established that bacteria can grow well on three of the four commonly used types of coating materials[1] and that the environment of the backfilled pipe line ditch is favorable for microbial activity,[2] the final phases of this project were undertaken. This involved detecting other physical alterations or changes of these coating materials which decrease their value as protective coatings.

With respect to cathodic protection, it is well to consider that the electrical insulating properties of a coating represent a single highly important factor. If electrical resistance is high and remains high, current needs and hence cathodic protection costs are low.

Laboratory tests are in progress under controlled environmental conditions to show that bacterial growth on coatings can cause loss of its insulating value. The relationship of moisture absorption and the presence or absence of cathodic protection on microbial development and coating resistance are also being investigated.

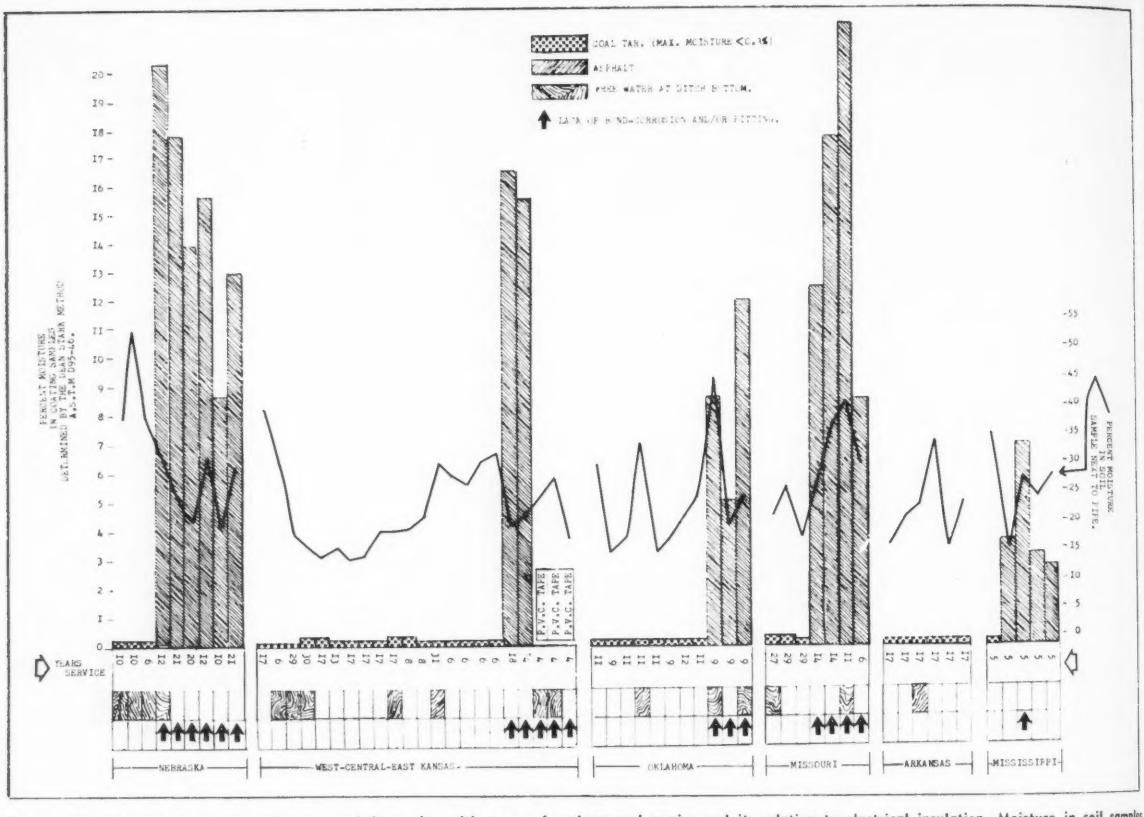

Figure 12—Moisture in coating samples removed from pipe with years of underground service and its relation to electrical insulation. Moisture in soil samples next to pipe at ditch bottom as is found along 90 percent of cross country right-of-way. Samples were from Nebraska, Kansas, Oklahoma, Missouri, Arkansas and Mississippi.

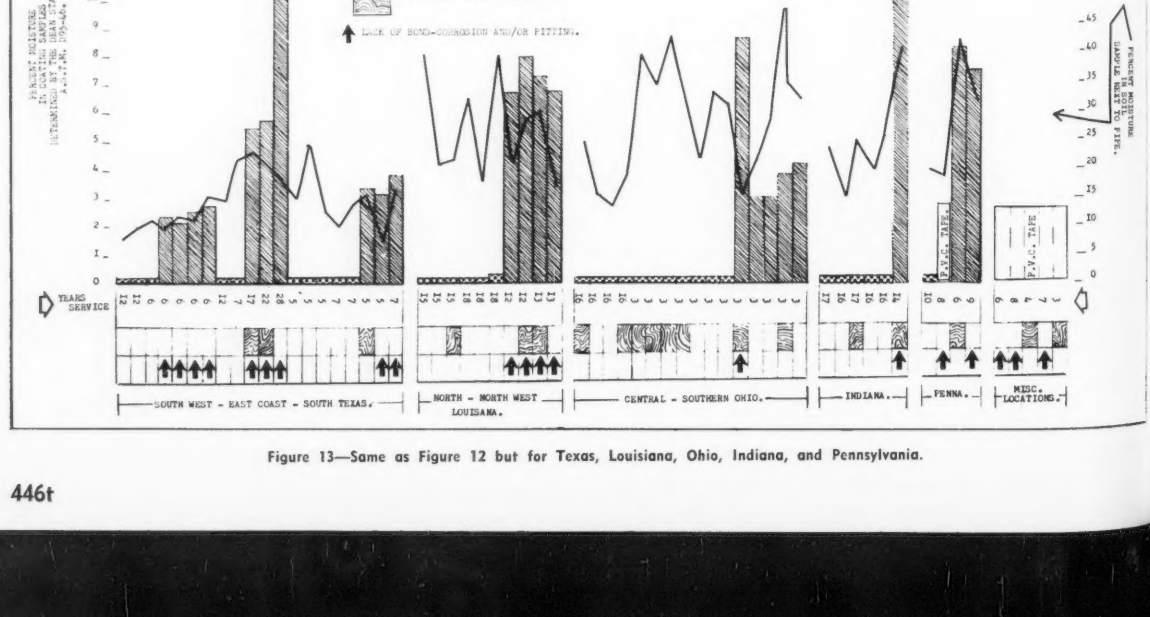

Figure 13—Same as Figure 12 but for Texas, Louisiana, Ohio, Indiana, and Pennsylvania.

Figure 14—Mobile field laboratory being used to facilitate pipe line microbiology research of the Kansas State University project.

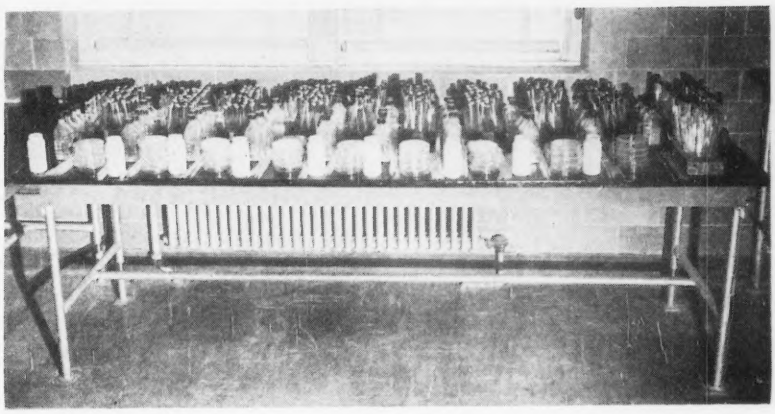

Figure 15—Amount of glassware used to make these analyses for one bell-hole from which is taken seven soil samples and two coating samples removed from the pipe.

Microbial Corrosion of Bare Metal

The theory of corrosion accelerated by the anaerobic sulfate reducing bacteria as proposed by von Wolzogen Kuhr[4] has been discussed in a number of reports. The work of Hadley[5] linking this group of bacteria to field observations of their corrosive action, the researches of Starkey and Wight[6] indicating hydrogen utilization by these bacteria, and the pioneering work of Starkey, Deuber,[7] Costanzo[8] and McVey[9] in the development of the "Redox-Probe" are familiar to most workers in the field of underground corrosion. By way of review, the fundamental reactions were as follows:

(A) $4Fe \rightleftharpoons 4Fe^{++} + 8e$

(B) $8H_2O \rightleftharpoons 8H^+ + 8OH^-$

(C) $8H^+ + 8e \rightleftharpoons 8H$ (polarizes metal surface)

(D) $H_2SO_4 + 8H \rightarrow H_2S + 4H_2O$ (depolarization)

(E) $Fe^{++} + H_2S \rightarrow FeS + 2H^+$

Reaction (D) represents the stage contributed by these specific microorganisms now called *Desulfovibrio desulfuricans*. These bacteria reduce sulfates to sulfides and at the same time oxidize the hydrogen depolarizing the metal surface causing the loss of more metallic iron to the ferrous form as represented by equation (A). These bacteria are strict anaerobes growing only in the absence of oxygen and under strictly reducing conditions. This property led to the development of a measure of the oxidation-reduction state of the soil as an indication of activity of sulfate reducers.

Because of the interest in this group of microorganisms and their activities, *Desulfovibrio desulfuricans* has been isolated from bell-hole soil samples studied during the past year. An electron microscope photograph of the bent rod form of *Desulfovibrio desulfuricans* is shown in Figure 16. This organism is probably of little or no significance in coating deterioration but would be an important factor in corrosion *under* unbonded or failing coatings or bare metals. Information regarding this group of bacteria is needed to evaluate fully their significance in corrosion problems especially as related to cathodic protection under a variety of environmental conditions.

While most attention has been focused on the sulfate-reducing anaerobes, the fact that other organisms of the soil may contribute to the corrosion process has been mentioned by a number of men including Hadley,[5] Starkey,[6] Kulman,[10] and others. Aerobic conditions combined with anaerobic or partially anaerobic zones at pipe line levels offer many possibilities for other types of microbial activity to influence corrosion. Since many bacteria form quantities of organic acids, the formation of many localized concentration cells would occur. In contact with metallic surfaces these would represent cathodic and anodic areas, setting up typical electrolytic currents.

While the main interest has been with coating deterioration, the finding of high bacterial populations adjacent to the coated lines together with indications of aerobic environmental conditions led to the conducting of a simple experiment to demonstrate concentration cell potentials of common soil bacteria in contact with steel. Common laboratory media (nutrient broth) was placed in two sterile containers at each end of a U-shaped steel rod one-fourth (¼) inch in diameter. One was inoculated, the other remained sterile. Bacterial growth products thus accumulated at one area of the metal while not at the other end. Platinum electrodes in contact with the culture solutions were connected to the proper instruments to indicate current flow or electrical potentials between the culture vessels. One such experiment is shown in Figure 17.

In all tests, differences in electrical potential could be measured. These varied depending on the culture, the time of incubation, and other conditions. Values obtained with 24 hour cultures were as follows:

Aerobacter aerogenes	0.256 v.
Bacillus cereus	0.383 v.
Pseudomonas aeruginosa	0.640 v.
Micrococcus parafinnae	0.555 v.

A complete circuit indicated a steady current flow over a period of two weeks which varied from 0 to 60 microamperes. The photograph shows the darkening of the liquid due to iron loss from the rod in the inoculated cell. The iron ions reacted with sulfur compounds present giving the typical FeS appearance.

The data from this experiment are presented merely to indicate one type of experimental study of a situation about which little is known either with respect to importance in field or laboratory conditions. No conclusions should be drawn from this single experiment except that this is an area which deserves attention from research workers in the field of microbiology in its relation to corrosion.

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DISCUSSION

Comments by F. E. Kulman, Consolidated Edison Co. of N. Y., New York City:

Dr. Harris' paper on the effects of soil micro-organisms on coating deterioration and on corrosion of bare metal is a contribution to a field of corrosion where much more work remains to be done. His contributions and those of other microbiologists have thrown light on certain fundamental aspects of deterioration and corrosion. The corrosion engineer is thereby enabled to select the most stable coatings for underground use and to specify and design his mitigative measures with greater surety.

Dr. Harris presents briefly the results of a short time experiment in which steel electrodes were immersed in inoculated and sterile nutrient media and potential differences in the order of 0.25 and 0.65 volt were measured. Such a laboratory test is a simple representation of a pipe line traversing various types of soil in which differences exist with respect to aeration, drainage, organic matter, bac-

Figure 16—Electron microscope photograph of the bent rod of *Desulfovibrio desulfuricans*. Approximately 23,000X.

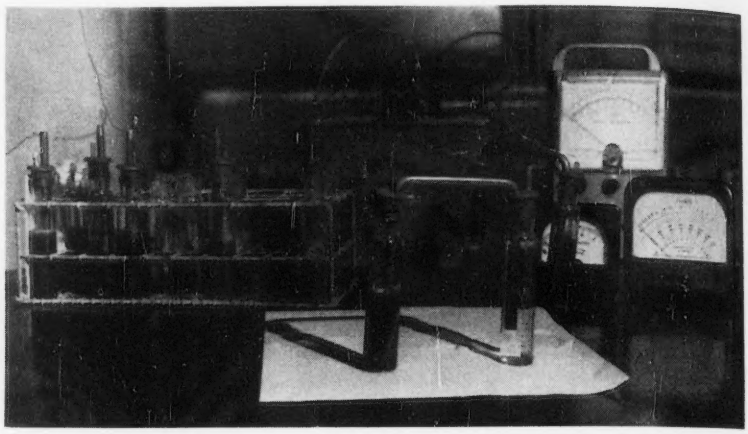

Figure 17—An experimental set-up of a U-shaped steel rod in a sterile and an inoculated culture, set up to measure the current and/or potential established by the concentration cell effects due to bacterial growth in the inoculated vessel. Note the dark color of the inoculated tube indicating the accumulation of corrosion products in three days' incubation.

terial population and other factors which may influence the corrosion process. A simple determination of the corrosion potentials of the soils can be made by means of the soil redox probe. Other things being equal, the soil with the lowest redox potential would be most corrosive. It is the opinion of this discussor that the driving force in underground corrosion at a particular point is related to the difference in redox potentials at that point and the remainder of the line.

Other investigators have shown that pipe line leaks caused by corrosion have tended to occur in soils of low resistivity. The correlation between leaks and soil resistivity has not been as good in the northeastern part of the United States as in the western states. This has led to a search for other indications of corrosiveness. Significantly, most of the investigations of bacterial corrosion have been undertaken in the northeast. Out of this work has come the measurement of the soil redox potential and its interpretation as a corrosiveness index in accordance with the scale proposed by Dr. R. L. Starkey.[1]

The limited experience with the soil redox probe in measuring soils around gas mains in New York City suggests that it will be possible to estimate, in at least a rough way, the probable rate of soil corrosion at all points along the pipe line where soil redox potential and resistivity measurements can be made. This estimation will be possible for bare pipe and for bare areas of coated pipe line. It should also be possible to make the estimate from measurements made before laying the pipe line if the proposed depths of burial were known.

With knowledge of the probable rate of corrosion available, the corrosion engineer should be in a much better position to proportion the cost and design of the mitigative measures to the actual corrosion hazards existing or expected.

Acceptance of the concept of the driving force being related to the difference of redox potentials should not exclude the possibility of other mechanisms operating at the same time. In soils undergoing periodic reduction and oxidation from varying water tables, for example, sulfates are reduced to sulfides and anaerobic corosion occurs during the reduction phase. During the oxidation phase, the sulfides are oxidized to sulfates and acidic corrosion occurs. Thus there is a regeneration of the sulfates and an interplay between anaerobic and aerobic bacteria. This mechanism was suggested by Von Wolzogen Kuhr[2] and oddly enough has been referred to by only a few workers in the corrosion field. It is conceivable that an exposure of pipe to such a cyclic condition might not be divulged by a single soil redox measurement but would require measurements over a period of time.

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Any discussion of this article not published above will appear in December, 1960 issue.

Interference With Railroad Signal Systems From Cathodic Protection Currents*

By FRANK L. CHATTEN

Abstract

The relationship of track circuits to railroad signal systems, and their construction and basic requirements to conform to Interstate Commerce Commission rules are reviewed. The need for freedom from outside influences is explained. Testing methods to detect interference with track circuits and corrective measures are covered. Known cases of past interference are reviewed. 8.9.4

Introduction

INTERFERENCE FROM cathodic protection may be described as the effect on one structure which results from the application of a cathodic protection system on a neighboring structure. The avoidance of such interference is the responsibility of the engineer who designs the installation for his own structure. When interference of this type between structures is involved the effects may require a period of years before severe damage eventually results. In the following discussion however the results may become apparent quickly and can have immediate devastating effects in the form of accidents.

Since 1870, railroad signal systems have been dependent upon a universal positive means for detecting the presence of a train upon a track. A closed electrical circuit scheme, using the rails of the track as a part of the circuit, was devised at that time and still forms the basis for all efficient signal systems. The 1958 Annual Report of the Interstate Commerce Commission[1] shows the railroads of the United States have a total of 110,689 miles of track equipped with automatic block signals for safe movement of trains. Each of the signals protecting the tracks is controlled by one or more track circuits.

In addition there are many highway grade crossings protected by automatic lights, gates or bells, involving the safety of the public, which are dependent upon track circuits for their proper operation.

All signaling systems on railroads in the United States are subject to rules and regulations issued by the Interstate Commerce Commission,[2] covering the installation, inspection, maintenance and repair of signal systems, devices and appliances. It is the purpose of these rules to require that signal systems be constructed and maintained to insure safety of train operation. These rules define a track circuit as "an electrical circuit of which the rails of the track form a part," and contain instructions which prescribe the requisites for construction and maintenance of signal systems with which all railroads must comply. Compliance with these rules requires that each track circuit must perform its proper function free of any outside interference.

Interference with track circuits from stray d-c foreign earth currents has long been a product of trolley lines and electric railways, a condition which has been known and guarded against by the railroad signal departments. The introduction of protective currents and anodes to provide cathodic protection for underground cables, pipes and other structures resulted in a new source of interference with railroad track circuits. Trouble from this new source was recognized in a report of the Association of American Railroads Signal Section[3] in 1943, covering the possibilities of improper signal operations due to cathodic protection for lead cable sheaths. As the use of cathodic protection systems expanded during the succeeding years the matter was again covered in a further report[4] in 1954.

About the Author

FRANK L. CHATTEN is System Engineer-Communications and Signals of The Pennsylvania Railroad, Philadelphia, Pa., in charge of construction and maintenance of those facilities. Following graduation in 1928 from Rutgers University with a BS in EE degree, he joined the Communications and Signals Department of The Pennsylvania Railroad. He is a member of the Association of American Railroads and AIEE.

Description of Track Circuit Operation

Track circuits are the most important link in a railway signal system as they provide the means whereby moving trains keep continuous control over the system. Figure 1 illustrates the simplest type of track circuit which is a continuously energized direct current circuit fed from a track battery. The battery may consist of primary cells having 0.6 to 0.9 volt output, or may comprise one or more storage cells having a charging rectifier to maintain their state of charge. A resistor is used between the battery and track to limit the flow of current, particularly when the track circuit is occupied by a train near the battery end of the circuit. The length of the circuit may vary from only a few hundred feet to as much as 6,000 feet, as circumstances dictate. Control of the signals, or other devices, is accomplished by a relay connected to the other end of the track circuit. The relay, on circuits of this type, usually has a low resistance winding of from 0.5 to 16 ohms. Low resistance relays are a better match for the longer track circuits and high resistance relays are better for the shorter track circuits.

Rail bonds, generally of wire, are connected around the rail joints as the rail joint bars alone do not always provide good electrical contact. Continuously welded lengths of rail which are used in some instances make the bonds unnecessary.

Each track circuit is separated electrically from the adjoining circuits by insulating joints which are installed in the rails.

If the track circuit is unoccupied, as shown in Figure 1, current from the track battery will flow through the limiting resistor, down one rail, through the track relay coils, and return through the other rail to the battery. This will cause the relay to close contacts controlling the signal and show the block is clear.

Figure 2 shows the track occupied condition. When a train enters the circuit, the wheels and axles provide a shunt across the track, ordinarily on the order of 0.0001 ohm. This is within the limits prescribed by the Interstate Commerce Commission rules, which require maintaining the track circuit so that the track relay will be in deenergized position if a shunt of as high as 0.06 ohm resistance is connected across the rails of the circuit.

The resistance of the shunt being low compared to the resistance of the relay, the major part of the current will flow through the train shunt, causing the armature of the track relay to release and the signal will show the block is occupied.

The Interstate Commerce Commission rules require each track circuit to operate on safe principles, so that the track relay will be deenergized if a train, locomotive or car occupies any part of a track circuit, or when a rail is broken or a rail is removed. Improper energizing of the track relay, such as might occur from a cathodic protection system, must be avoided at all times. To meet such requirements the corrosion engineer

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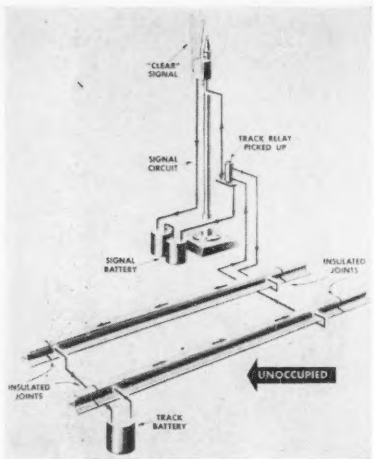

Figure 1—Clear track. Current flows through rails of entire section from battery to relay.

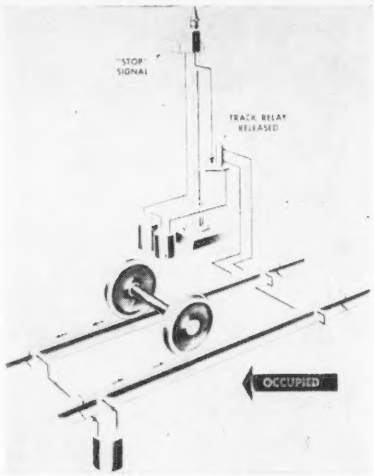

Figure 2—Track not clear. Current flows through rails to wheel shunt but not to relay.

must design a system in conjunction with related properties that will eliminate the corrosion on his property without causing harm to the property of others.

Effects of Cathodic Protection on Track Circuits

Cathodic protection systems can be the cause of harmful effects on railroad signals which will show themselves in either of two undesirable conditions. The first may cause a signal to needlessly stop trains and is therefore called a false restrictive signal. While this may seem to be merely an unfortunate situation, it cannot be dismissed too lightly. The stopping of a train costs the railroad money, and any delay will be reflected in delayed connections with other trains on the same or another railroad.

The second condition, and by far the worse of the two, may cause a signal to indicate to an engineer that a block is clear when it is actually occupied by another train. This is a dangerous situation which might result in a collision. The Interstate Commerce Commission requires each railroad to make special reports of all such false proceed failures. This condition may result in personal injury or death to passengers, and serious property damage.

How Cathodic Protection Systems May Cause Interference

As described above, the track circuit would appear to be rather simple in operation but this is complicated by weather conditions. Dry weather is of no concern. In wet weather there may be considerable leakage from one rail to the other through the ballast and across the ties, the amount of leakage depending upon the nature of the ballast (whether stone, cinders, etc.). This leakage path provides a circuit for the possible flow of current from a cathodic protection system into the rails. Figure 3 illustrates how this occurs. The rectifier current which is discharged through the ground bed to the earth, flows through the earth into the rails.

In Figure 3 the resistance of the path through the ties and ballast, and from the ballast to earth, is represented by a number of resistors. In an actual track circuit the ballast resistance is distributed throughout the length of the circuit since there are many paths due to cinders, dirt, etc. touching the base of the rails and filling cracks in the ties. This resistance changes with the weather conditions. Under normal conditions with the bonding on each rail in good order, and with the resistance of each rail to ground being the same, the current from cathodic protection would flow down each rail in the same direction and not affect the operation of the track circuit. However, if one rail should have lower resistance to ground than the other, the current would not be balanced and the track relay might be falsely energized.

It is under the unusual conditions, which result from a broken rail or broken bond wire, that a circuit condition is set up which may permit the false energization of the track relay from a cathodic protection system. The diagram of Figure 3 shows how the current from a buried anode enters the rails from the ground and produces a current flow through the track relay. The existence of false track relay current can be determined by a few simple tests.

Detection of Interference

In order to determine if any energy is being introduced into a track circuit from a cathodic protection system a series of comparative tests of track relay current should be made with the cathodic protection current on and off, preferably in some predetermined timing sequence so that its effect will be readily discernible on a meter. It is necessary to do this during wet weather conditions as the tests will be of little value when the resistance of the track ballast is high, as it is in dry weather. These tests should be conducted with the cooperation of all interested parties. The procedure for testing, simulating the condition of a broken rail or broken bond wire, consists in the removal of one set of rail joint bars and the rail bond from a joint at the center of the track circuit, to provide an opening in the circuit of one rail, as shown by Figure 4. Comparative tests are then made by the following procedure:—

TABLE 1—Currents in DC Track Relays

Relay Resistance, Ohms	Release Current, Amps	Pick-Up Current, Amps
4	0.027	0.054 to 0.067
2	0.040	0.080 to 0.100
1	0.054	0.108 to 0.135

1. With the track battery connected to the track circuit, as shown by Figure 4, the current to the track relay is measured under the following conditions:

A. *Track Unoccupied*

(1) With cathodic rectifier supply open.

(2) With cathodic rectifier supply closed.

B. *Track Shunted at the Battery End.*

(1) With cathodic rectifier supply open.

(2) With cathodic rectifier supply closed.

2. With the track battery disconnected from the track circuit.

Repeat A and B above.

Then the rail joint bars, and the rail bond, are replaced and tests with the track battery connected, as in Step 1, above, and with the battery disconnected, as in Step 2 above, are repeated.

Interpretation of Test Results

If the connection of the cathodic rectifier supply causes any change in the relay current which was measured without the rectifier connected, this is an indication of an interference condition which should be investigated. An idea of the amount of current which will prevent a d-c track relay from releasing is given in Table 1, in which it will be noted that 0.027 ampere will hold a modern 4-ohm track relay; 0.040 ampere will hold a 2-ohm relay, and 0.054 ampere will hold a 1-ohm relay. The relay pick-up currents may be from 2 to 2½ times these values.

From the preceding discussion it must not be concluded that the only form of track circuit which is in use is the simple d-c type which has been described. There are other kinds of d-c track circuits just as there are also a-c track circuits of various types, and combinations which employ a-c on the track with a rectifier feeding a d-c relay. A typical simple a-c track circuit is illustrated in Figure 5 in which a transformer feeds the circuit to which an a-c relay, either of a vane type or a motor type, is connected. Track circuits of this kind are not likely to be affected by cathodic protection currents. However, the a-c track circuit which employs the rectifier and d-c relay, is quite susceptible to false operation from cathodic protection systems, as shown by Figure 6. In

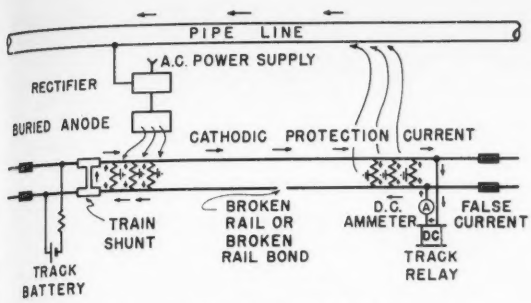

Figure 3—Interference current through track relay.

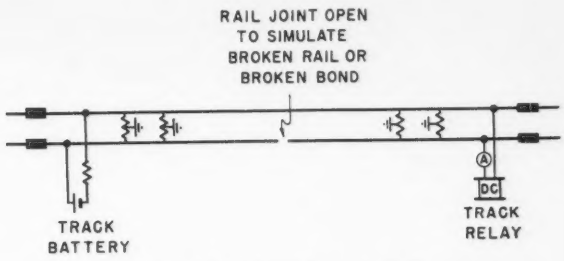

Figure 4—Interference test basic set-up.

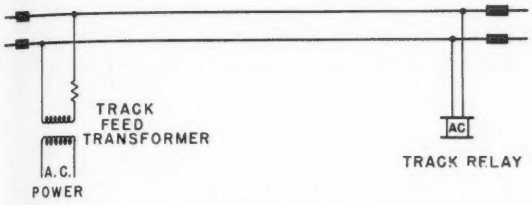

Figure 5—Typical AC track circuit.

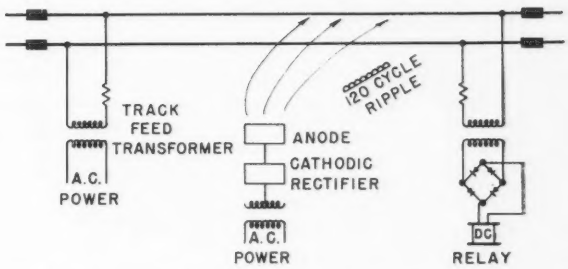

Figure 6—Interference current from rectifier ripple, rectified AC track circuit.

this instance, if the cathodic protection full wave rectifier is energized from a 60 cycle supply, there may be sufficient 120 cycle ripple to cause an unsafe interference current even though the track circuit rectifier and d-c relay are insulated from the rails by a transformer. A simple filter in the cathodic protection rectifier would minimize this ripple current, but if the filter circuit became open due to a broken wire or open condenser the possibility of false energization of the track relay from the ripple would still exist.

There are also in use d-c and a-c track circuits which, if interfered with by strong foreign direct currents, will fail in a safe manner. These are known as "Coded" track circuits wherein the energy feeding the circuit is interrupted periodically in accordance with a code pattern and frequency. The code patterns comprise one or more codes each consisting of a predetermined rate of energy interruptions per minute in practically even "on" and "off" periods. The track relay follows the code as pictured by Figure 7.

Interference from an outside source will affect the action of the track relay following the code, causing it to operate erratically or not at all, resulting in a failure on the safe side since this will cause the signal to show "Stop." This provides the benefit of detection of the interference as immediate investigation of the signal failure will disclose the interference.

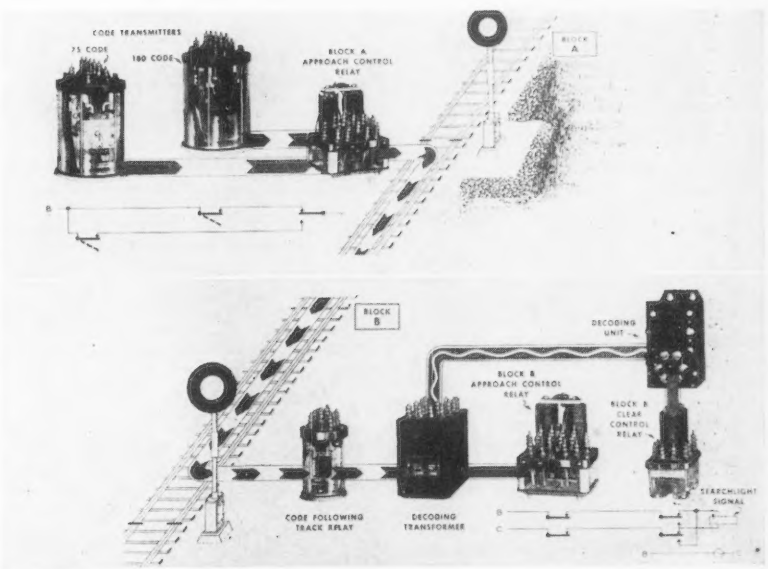

Figure 7—Coded track circuit control.

Elimination of Causes of Interference

The tendency of a cathodic protection installation to produce stray currents depends upon the location of the anode or anodes with relation to the track, the configuration and resistance to earth, the amount of protective current used, and the nature of the structure being protected (whether bare, poorly coated or well coated.) The application of a good coating during construction will be of great assistance in the elimination of interference. The cathodic protection anode should be placed as far away from the tracks as possible and located so that the structure being protected is between the anode and the track.

In some instances a large protective current is applied at one location with the objective of reaching out to protect other points some distance away. The strong current effect resulting from this practice can be minimized by using several smaller currents applied at intervals to provide more uniform coverage. The use of insulating joints or flanges in the pipe line or cable sheath will also help to minimize interference. Every means of avoiding the stray currents from entering the rails should be given consideration. A railroad track will generally be found to afford a lower resistance path than the surrounding earth and consequently may provide a better path for current from a cathodic system to enter the rails and flow to some other point rather than through the earth. The nature of the ballast condition, and frequently brine drippings from refrigerator cars, affect this situation.

In some instances there may be a temptation to use the rails of non-track-

circuited lines for cathodic protection system grounds. This may lead to interference where a track circuit abuts the non-equipped track because the wheels of a train may bridge the insulating joints between them and permit the current to improperly energize the track relay. Such connections should not be made without careful investigation and the approval of the railroad concerned.

Reported Cases of Interference

Six years ago a poll of 61 railroads was made to obtain information regarding interference experienced by railroad signal track circuits from stray current from cathodic protection on underground pipe lines, lead-covered cables paralleling the railroad, or other underground structures adjacent to railroad's rights-of-way. This poll developed the following information:

Forty roads reported cathodic protection having been installed and 5 roads reported 7 cases in which cathodic protection had interferred with track circuit operation. Correction was accomplished in two instances by relocating the anodes at greater distances from the track (as much as 1 mile) and in another by adding multiple grounds. In two other cases the d-c track relays were changed to a different type, in another case the track circuit was changed to a-c, and at one location the rectified current was lowered together with reversing the feed and relay ends of the track circuit.

Cooperative Joint Tests

The poll of railroads further indicated 13 roads had made joint field tests with a representative of the owner of the cathodic protection. The importance of cooperation between the owners of cathodic protection installations and the railroads cannot be too strongly emphasized, particularly since the railroads are required by the Interstate Commerce Commission to install and maintain their signal systems in a safe condition to avoid injury or loss of life, and damage to property. The corrosion committees which operate in various localities provide an excellent means for cooperative action. The importance of notifying the railroads, adjoining whose lines new installations, or changes in existing systems are to be made, is of great value to them. They will then have the opportunity of determining at its inception, the possible effects of a new installation on the railroad signal system in the area.

Conclusions

The track circuit has long been a fundamental tool of railroad signal systems and there is an increasing number of functions which track circuits perform. Automated train operation can be provided by track circuits through inducing signals on the train for indication and control. The future points up many possible further uses of track circuits and thus a basically simple device is becoming more complicated through multiple purposes. This makes it all the more necessary that interference from outside sources be avoided.

The question may be raised as to the possibility of the converse situation arising whereby track circuits might cause adverse conditions on unprotected underground pipes and cables. Due to the very low voltages and currents involved in track circuits no conditions of this nature have ever been developed.

In this discussion the need for cooperation between the signal departments of the railroads and the corrosion engineers has been stressed. It is only through the joint efforts of these two groups that satisfactory results will be attained.

Acknowledgement

The assistance received from the staff of the Union Switch & Signal Division of Westinghouse Air Brake Co., Swissvale, Pa., is gratefully acknowledged.

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2. Interstate Commerce Commission, Bureau of Safety, Rules, Standards and Instructions for Installation, Inspection, Maintenance and Repair of Automatic Block Signal Systems, Interlocking, Traffic Control Systems, Automatic Train Stop, Train Control and Cab Signal Systems, and Other Similar Appliances, Methods and Systems, October 1, 1950.
3. Proc. AAR Signal Section, 153-A - 154-A (1943).
4. Proc. AAR Signal Section, 79A - 83A (1954).

DISCUSSION

Question by John M. Petkousek, Carlsbad, New Mexico:

Is a pipe line buried beneath a railroad switch yard endangered from stray current from DC signal equipment either in normal operation or under abnormal conditions? The pipe line was not under cathodic protection in this area, and coating is partially deteriorated.

Reply by F. L. Chatten:

The nature of the yard is not stated. If it is a yard having switches operated from one or more control points, a track circuit is usually provided in the vicinity of each switch to prevent the switch being thrown while a car is approaching or on it. Other yards which have switches operated by hand do not need track circuits. In any case, the low voltage and low current of each track circuit should have no effect, under any condition, on a pipe buried in the vicinity.

If suspicions of the condition described continue, a field investigation may then be in order.

Question by Lance F. Heverly, Toronto, Ontario, Canada:

Is it always necessary to use a shunt across the track when checking interference under a simulated broken rail condition?

The reason for my question was to cite an example whereby it was not necessary to provide a shunt across the track circuit so as to demonstrate the ill effects of a rectifier ground bed being placed too close to railroad tracks. In this instance, one rail was separated by an insulated joint so as to simulate a broken rail condition. With the rectifier de-energized, the nearby semaphore arm dropped down, the road gate dropped down at a nearby road crossing, the caution lights were flashing and a bell was ringing. When the rectifier was energized the semaphore arm went back to its normal vertical position, the gate at the road crossing raised, the lights went out and the bells stopped ringing. If we used a shunt across the track circuit, I was wondering whether or not these adverse effects of the rectifier would be so aptly demonstrated.

Reply by F. L. Chatten:

In the instance described the opening of the rail circuit by the insertion of an insulated joint interrupted the normal flow of current through the track relay which caused the highway crossing protection to operate and the signal to indicate the improper condition which simulated a broken rail. Introduction of the cathodic rectifier interference current then energized the track relay falsely. With the rail circuit open a shunt across the rails at the battery feed would not shunt the relay. The testing procedures described in the paper include four tests made with a shunt applied at the battery feed end of the track circuit, and four to be made without the shunt so that the effects of the rectifier will be detected under at least one of the test conditions. Consequently a shunt across the track is not always necessary.

In this case, the effects point to a very severe case of interference which was easily detected without making the detailed tests suggested. These tests will detect conditions which, although of much less severity, could result in dangerous conditions in the signal system.

Any discussion of this article not published above will appear in December, 1960 issue.

NATIONAL ASSOCIATION of CORROSION ENGINEERS

Service Life of Pipe Exposed to Domestic Waters

A Status Report of NACE Unit Committee T-4E* On Corrosion by Domestic Waters

NACE TECHNICAL COMMITTEE REPORT

Publication 60–11

Abstract

Tests were made to determine the effect of domestic waters of various qualities on eighty-six 24-inch pipe specimens. Pipe materials evaluated include galvanized iron, black iron, aluminum and copper; exposures of these metals were made in both hot and cold water service. Data reported on waters used in tests include source of water, temperature, water analyses, pH, dissolved oxygen, Saturation Index, Ryznar Index, flow and pressure.

It was found that black steel was not satisfactory for normal service use. Aluminum was not resistant to waters containing copper salts or with a pH less than about 6-6.5. The presence of copper ions in water appeared to be detrimental to galvanized iron. 4.6.6

Introduction

THIS STUDY was made to establish the corrosivity of several public water supplies to metals ordinarily used for domestic and institutional service pipe. The proposal to carry out this work was made to the commitee in 1955 by the chairman and by two steering committee members, J. F. J. Thomas and H. L. Shuldener. Encouraging replies were obtained from three members of T-4E and participation pledged by five, one of whom was unable to complete participation.

Eighty-six 24-inch pipe specimens were installed in a number of American and Canadian service lines handling hot and/or cold water of 30 different qualities. The types of metal pipe used are given in Figures 1 and 2.[1] The time of exposure was designed to be two years. The actual exposure times are indicated under the "Flow" column in Table 1 under "Yrs."

These specimens were examined by the participants and shipped to the chairman with analytical and other pertinent data and comments.

The specimens were again examined and a representative four-inch length which was cut from each specimen was then split in two. One half was cleaned by an accepted procedure and both halves were sprayed with a transparent acrylic spray.

These sections were then mounted on two plywood boards, one for cleaned (Figure 1) and one for uncleaned specimens (Figure 2). Specimens were mounted more or less in the order of decreasing excellence of visual appearance with the cleaned galvanized specimens (exposed to cold waters) used as a standard. Cold and hot galvanized iron, black steel, aluminum,[2] and copper were mounted in vertical rows in this order. Horizontally, specimens were mounted so that metals tested in common quality waters would be aligned.

No attempt was made to measure pit depths or weight loss since the study was designed to indicate only whether or not corrosion occurred. Admittedly, some borderline cases between a "yes" and "no" answer were possible, but from the specimens under study no such cases were evident.

The analytical data were summarized with additional pertinent data and comments and tabulated in Table 1.

Summary of Analytical Data

For surface (lake or river) waters, the median quality was indicated as representative rather than the range. The range was greater for river waters than for lake waters but in each case the proportion of the ions was generally similar. For surface waters, the dissolved oxygen was indicated to be at saturation unless marked otherwise; for well waters the dissolved oxygen was indicated as trace unless aerated or otherwise indicated.

The pH reported was assumed to be for 25 C, by empirical conversion within the instrument.

The Ryznar Index[3],[1] was calculated from the reported pH and the index value was indicated to be +++, for waters for calcium hardness of zero to 10 ppm, since for the alkalinities reported there is no pH at which calcium carbonate can precipitate and therefore this factor has no significance.

The saturation index[4],[2] was calculated for the various supplies for the *temperature of exposure* by correcting[3] the reported pH to that at the exposure temperature and calculating pH_s for each temperature. For waters of zero to 10 ppm calcium hardness the saturation index was indicated as —.

The flow rates were metered at La-Verne, Ottawa, and Kingston (Al Co). All other reported rates were estimated.

Analytical Data vs. Appearance

1. Galvanized Iron

There is no way that the cleaned specimens can be evaluated on a relative basis.

(a) No rust spots showed on cold water specimens from Denver (Marston) or on any specimens mounted above it in Figures 1 and 2. Pitting was evident in a somewhat increasing magnitude on specimens from Denver (Moffat) and below in these figures.

At the London location the cold water exposure in a copper line to a drinking fountain was insulated from the copper. However, copper was still noted in the analyses of the water.

The Halifax (Spruce Hill) supply reported no alkalinity with a pH of 4.2 to 6.2.

(b) No rust spots showed on hot water specimens at Manteno or above. Pitting in varying degrees of magnitude was noted at Quincy and below.

2. Black Steel

Of particular interest was the unsatisfactory appearance of black steel. All specimens showed pitting of various types and degrees as well as tuberculation. In fact the Halifax, Ch.L. specimen almost plugged.

(a) The best specimens from a standpoint of appearance were those in cold water at Lindsay (city) and at Dwight.

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* T. E. Larson, Illinois State Water Survey, Urbana, Illinois, chairman of this committee at the time this report was prepared. The working task group for the collection of the data were G. E. Burnett, Bureau of Reclamation, Denver, Colo.; R. W. Lane, Illinois State Water Survey, Urbana, Ill.; Lee Streicher, Met. Water Dist. of So. Cal., La Verne, Calif.; J. F. J. Thomas, Dept. Mines and Tech. Surveys, Ottawa, Ont.

[1] In addition, cast iron, wrought iron, and red brass specimens were exposed to cold and hot water at Denver (Marston and Moffat supplies).

[2] Not Alclad aluminum.

[3] Index = 2 pH_s-pH, where pH_s is the calculated pH of saturation with respect to the calcium carbonate, and pH is the determined pH at 25 C.

[4] Saturation index = pH-pH_s, where pH_s is the calculated pH of saturation with respect to calcium carbonate at the temperature of use, and pH is the determined pH at this temperature.

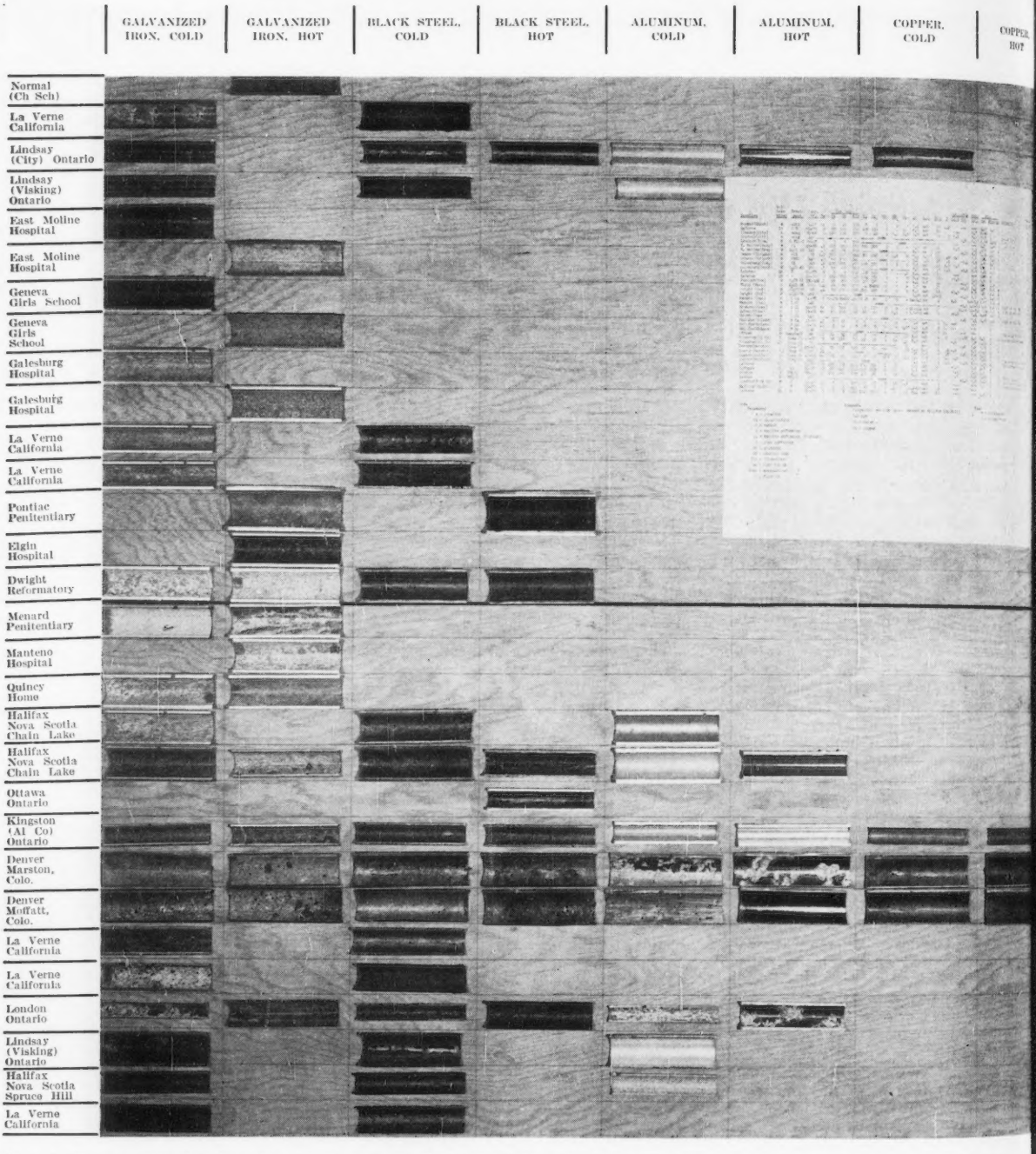

Figure 1—Pipe exposed to domestic waters (cleaned specimens). The terms "hot" and "cold" at top refer to the water service to which metals were exposed.

(**b**) Glossy uncorroded areas were evident on specimens in hot water at Lindsay (city), Pontiac, London, and to a lesser extent for Halifax (Chain Lake). There appears to be no feature of water quality which may account for this localized condition.

3. Aluminum

All aluminum specimens looked good except Denver (Marston and Moffat), London, and Halifax (Spruce Hill). The last named specimen showed general corrosion by *virtue of the low pH* whereas the others were pitted as the result of exposure to copper-bearing water.

(**a**) At the end of the first year at Denver, tubercles were found only in the cold water exposures of aluminum.

(**b**) At the end of the second year, the pitting and tuberculation was severe in the hot water exposure to the Marston supply as well as at both cold water exposures. Copper sulfate was used for algae control (1-1.5 pounds per million gallons) at both reservoirs.

4. Copper

The few copper exposures evaluated all appeared to be in good condition. No attempt can be made to suggest water quality which may be destructive to this type of pipe. This does not imply that copper pipe is universally superior to other types. It is well known that under some conditions of use, copper pipe will fail with many waters. And for some waters, failures of this material will occur in time under normal conditions of domestic use.

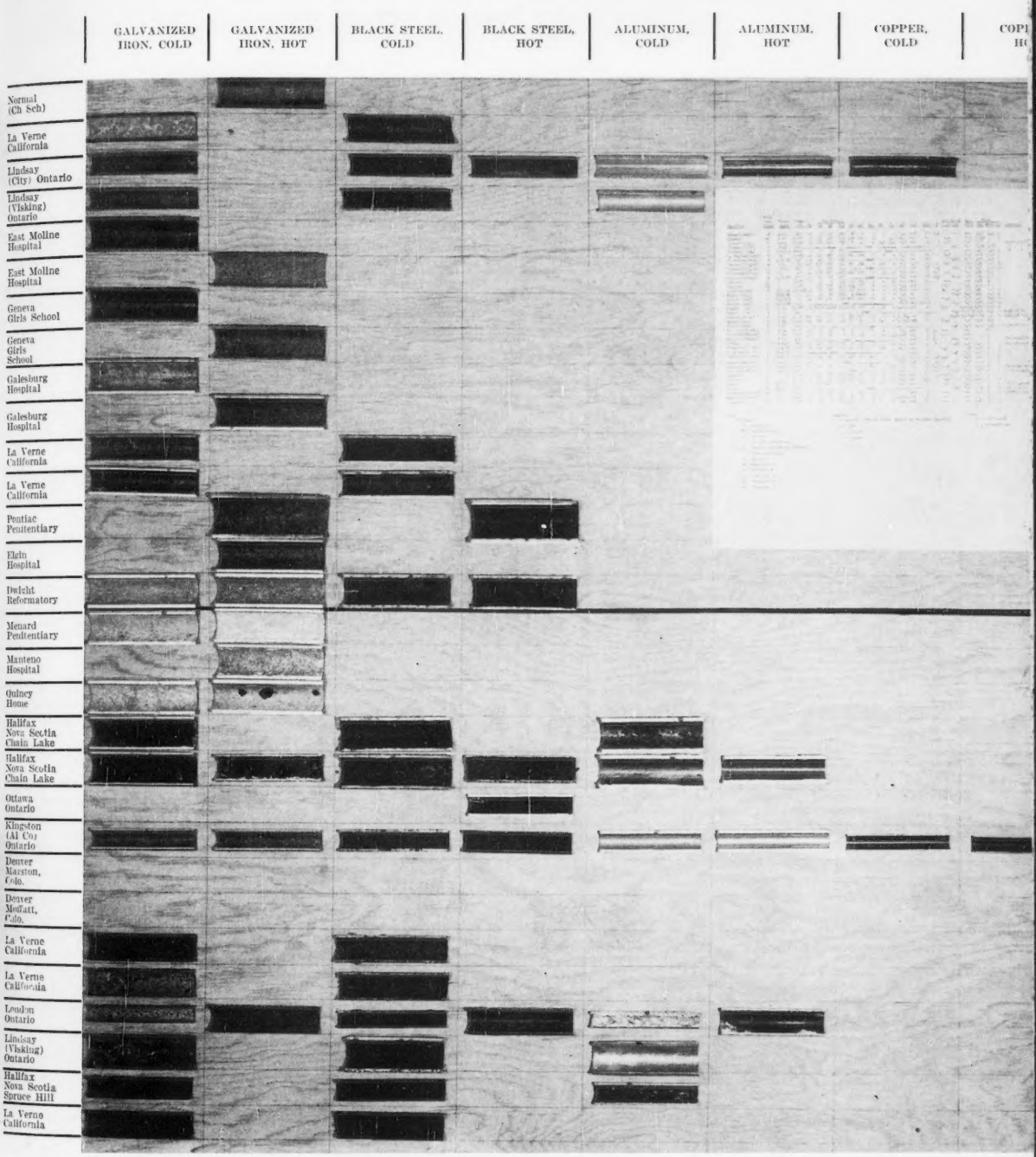

Figure 2—Pipe exposed to domestic waters (uncleaned specimens). The terms "hot" and "cold" at top refer to the water service to which metals were exposed.

Saturation Index Analysis

1. Galvanized Iron

(**a**) A positive saturation index is not always a guarantee that rust spots will not develop on galvanized iron within two years. The relative position of the Ottawa water should perhaps be lowered in the visual rating, since no galvanized specimens were available for inspection. However, in the absence of a positive index, corrosion occurred in all but a few samples. The waters with a negative index in which corrosion did not take place are shown by ϕ in Table 1.

(**b**) The specimens exposed to the two LaVerne waters with a positive index illustrate the influence of quantity of water on corrosion. Galvanized iron corroded when the flow was at a constant rate of 5 gpm (4.7 million gallons total) but did not corrode when the flow was intermittent at 5 gpm (0.3-0.5 million gallons total).

(**c**) It is perhaps most significant that in every instance where treatment was adjusted by sodium silicate or caustic soda to a positive saturation index, the treatment was successful.

(**d**) The 175 F temperature at the hot water exposure at Kingston may be the cause of pitting, even though the saturation index is quite high.

2. Black Steel

A positive saturation index did not appear to benefit the black steel exposures.

TABLE 1—Exposure of Pipe to Domestic Waters

Location	Well, Lake, or River	Treatment[1]	Temp., Degrees	WATER ANALYSES Fe	Ca[2]	Hd[2]	Alk[2]	Cl	SO_4	Cl_2	pH	DO[3]	SiO_2	F	SAT. INDEX Cold	Hot	Ryznar Index 25 C	FLOW[4] mg.	Yrs.	i. c	Comments	Press, psi
Normal (ChSch)Ø	W	AZCl	140°	Tr	6	10	350	8	6	+	7.3	Sat	17	1.2	.....	———	+ + +	0.17	1.0	c		75
LaVerne	LR	Z_B	51–77	0	87	145	114	109	353	1.	8.5	Sat	10	....	+ .4	.....	7.3	0.50	2	i		38
Lindsay (City)	R	Coag*	35–68	Tr	150	190	150	7	40	0.3	7.7	Sat	4	0	+ .5	.....	7.3	0.7	2	i	(Cu tr) (color 10-30)	75
Lindsay (City)	R	Coag-Cl	140	Tr	150	190	150	7	40	0.3	7.7	Sat	4	0	+ .5	+1.4	7.3	0.05	1.65	i	(Cu tr) (color 10-30)	75
Lindsay (Visk.)Ø	R	Coag Cl Z	39–68	0	7	8	150	7	40	0.3	7.7	Sat	4	0	———	.....	+ + +	1.5	0.9	c	(Cu tr) (color 10-30)	75
E. Moline (Hosp)	W	Cl	45–56	.1	215	380	250	550	300	+	7.3	Tr	16	....	0.0	.....	7.3	0.05	1.9	i		35
E. Moline (Hosp)	W	Z_BCl Si	140	.3	40	76	250	550	300	+	8.0	Tr	20	....	.....	+1.0	8.0	0.05	1.9	i		35
Geneva (Girl, Sch)	W	—Cl	55	1.0	300	550	344	80	150	+	7.3	3.0	15	.3	0.0	.....	7.6	0.24	1.9	c		45
Geneva (Girl, Sch)	W	Z_BCl	140	.3	60	100	344	80	150	+	7.2	3.0	15	.3	.....	+0.1	7.9	0.35	1.9	i		45
Galesburg (Hosp)	W	Cl	60	.2	170	290	250	200	575	+	7.6	Sat	11	2.0	0.0	.....	7.2	0.53	2.0	i		45
Galesburg (Hosp)	W	Z_BCl Si	160	.1	35	60	260	200	575	+	8.1	Sat	17	2.0	.....	+0.6	7.7	0.21	2.0	i		45
LaVerneØ	LR	Z	51–77	0	5	9	112	112	353	.2	8.4	Sat	10	....	———	.....	+ + +	0.28	2	i		25
LaVerne	LR	.....	51–77	0	232	372	120	104	353	0	8.4	Sat	10	....	+0.7	.....	6.6	0.32	2	i		25
Pontiac (Pen)	R	Z_BCl Si	130–180	.1	45	80	210	20	120	+	8.1	Sat	14	....	.....	+1.0	7.3	1.84	1.3	i		50
Elgin (Hosp)	W	Z_BCl Si	130	1.4	45	80	270	4	30–200	+	7.5	Tr	15	.8	.....	+0.0	8.3	0.48	2.5	c		50
Dwight (Ref)	W	AZ_BClOH	60	.4	55	100	270	375	225	+	8.3	Sat	13	....	+0.3	.....	7.7	0.10	2.2	i		50
Dwight (Ref)	W	AZ_BClOH	160	.4	55	100	270	375	225	+	8.15	Sat	12–21	....	.....	+1.0	7.7	0.56	2.2	c		50
Menard (Pen)	R	L Cl	34–78	0	70–150	80–200	45–130	20	80	+	8.4–9.3	Sat	4	....	+ .6	.....	6.6–7.3	1.60	2.2	c		65
Menard (Pen)	R	L Cl	140	0	70–150	80–200	45–130	20	80	+	8.4–9.3	Sat	4	....	.....	+1.1	6.6–7.3	0.82	2.2	i	High pH vs. Mg	65
Manteno (Hosp)	R	L Cl	140	Tr	65	100	35	25	110	+	9.3–10.1	Sat	10	....	.....	+1.0+	7.1–8.9	0.84	2.3	c	High pH vs. Mg	50
Quincy (Home)	R	L Cl	33–68	Tr	60	100	45	20	50	+	9.0–9.5	Sat	6	....	+0.3	.....	7.5	0.68	3.1	i		60
Quincy (Home)	R	L Cl	140	Tr	60	100	45	20	50	+	9.0–9.5	Sat	6	....	.....	+ .6	7.5	0.33	3.1	i	High pH vs. Mg	60
Halifax (Ch. Lake)Ø	L	F Ca	33–70	.1	9	12	8	6	6	—	7.2	Sat	2	1.	———	.....	+ + +	.....	2	c		...
Halifax (Ch. Lake)Ø	L	F $CaCl_2$	33–70	.1	9	12	8	8	6	0.35	6.8	Sat	3	1.	———	.....	+ + +	.....	2	c		...
Halifax (Ch. Lake)	L	F $CaCl_2$	125	.1	9	12	8	8	6	0.35	7.0	Sat	3	1.	.....	———	+ + +	.....	2	.....	(Cu 0-0.4) (color 25)	...
Ottawa	R	CoagCaCl	156	Tr	42	50	23	3	25	—	8.0	Sat	4	0	.....	— .35	9.8	0.3	2	i	(Cu hotwater tank)	...
Kingston (Al Co)	L	Coag Cl	43–72	Tr	98	128	90	22	28	.2	8.0	Sat	1	0	+ .2	.....	7.8	0.03	2	i	Cu trace	20
Kingston (Al Co)	L	Coag Cl	175	Tr	98	128	90	22	28	0	8.0	Sat	1	0	.....	+ .8	7.8	0.03	2	i	Cu trace	20
Denver (Marston)Ø	L	Coag Cl	45–63	.1	74	116	123	35	51	.05	7.3	8.0	4	.8	— .9	.....	8.5	0.43	2	i	Cu SO_4 treatment	95
Denver (Marston)	L	Coag Cl	190	.1	74	116	123	35	51	.05	7.6	2.8	4	.8	.....	+ .6	8.5	0.43	2	i	Cu SO_4 treatment	95
Denver (Moffatt)	R	Coag Cl	45–63	Tr	28	38	43	5	17	.11	7.4	7.6	4	1.0	— 6	.....	8 0	0.19	2	i	Cu SO_4 treatment	45
Denver (Moffatt)	R	Coag Cl	145	Tr	28	38	43	5	17	.11	7.3	4.7	4	1.0	.....	+ .25	8.0	0.09	2	i	Cu SO_4 treatment	45
LaVerne	LR	.....	51–77	0	232	372	120	104	353	0	8.4	Sat	10	....	+0.7	.....	6.6	4.7	2	c		25
LaVerne	LR	Z_B	51–77	0	87	145	114	109	353	1.	8.5	Sat	10	....	+ .4	.....	7.3	4.8	2	c		38
London	W	NH_2Cl	55–60	.1	180	250	200	8	55	+	8.1	2.2	6	....	+ .8	.....	6.5	0.67	2	c	(Cu = 0.4–.8)	35–90
London	W	NH_2Cl	120	.1	180	250	200	8	55	+	8.1	2.2	6	....	+ .8	+1.2	6.5	0.12	2	c	(Cu = tr to 0.2)	35–90
Lindsay (Visking)	R	Coag Cl Z	35–40	.1	7	10	150	7	40	.3	.....	Sat	3	....	———	.....	+ + +	6.3	2	c	(Refrig) (color 10-25)	.....
Halifax (Spr. Hill)	L	F	33–70	.1	2	5	nil	6	5	—	4.2–6.2	Sat	2	1.2	———	.....	+ + +	.....	2	c		...
LaVerne	LR	Z	51–77	0	5	9	112	112	353	.2	8.4	Sat	10	....	———	.....	+ + +	4.6	2	c		25

[1] Code Treatment: A = aeration; Cl = chlorination; Z = zeolite softening; Z_B = zeolite softening (blended); L = lime softening; Si = silicate; OH = caustic soda; Ca = lime for pH control; Coag = coagulation and filtration; F = fluoride; Ø = locations where no corrosion of galvanized iron occurred in the absence of calcium carbonate protection (Neg. Sat. index).

[2] As $CaCO_3$.

[3] Dissolved Oxygen.

[4] Flow: mg = million gallons; c = continuous; i = intermittent.

* unfiltered

Comments: Manganese zero or trace except at Halifax (Sp. Hill) 0.1 ppm; Nitrate less than 1 ppm except at Elgin (6ppm), Kingston (.3—2.5ppm), London (5ppm); Ammonia less than 1 ppm except at Normal (2ppm).

3. Aluminum

There was no relation between corrosion of aluminum and the Saturation Index.

Other Factors

1. The Ryznar Index (Index value < 6 causes scale; > 7 causes corrosion or red water) does not appear to be too significant for galvanized iron on the basis of these examinations.

2. High alkalinity (over 100 ppm) is associated with good behavior toward galvanized iron, particularly with respect to hot water.

3. Silica in concentrations of 10-20 ppm was also generally associated with satisfactory performance of galvanized iron.

4. Soft water at Lindsay (Visking) appears more detrimental to galvanized iron when refrigerated to 35-40 F than when used at tap temperature. However, twice as much water was used per year in the former case through 1-inch pipe (2.5 ft/sec for 2 years) as in the latter case with ½-inch pipe (4.9 ft/sec for 0.9 year). Therefore, aside from the temperature, the *quantity* of water (as with the LaVerne samples) seems more important than the velocity.

5. Other observations at Denver showed (1) red brass was unaffected by either water, (2) cast iron was rather uniformly corroded and had thick corrosion products with both waters, (3) wrought iron was more severely pitted than black steel or even aluminum.

Conclusions

1. The variety of specimens evaluated was too small and in addition an inadequate number of installations was checked. More emphasis could have been placed on low mineral content waters such as found along the eastern sea coast.

2. In no case was black steel satisfactory for normal service use.

3. Galvanized iron surpasses black steel for certain waters, particularly because the simple application of caustic or silicates can easily be made relatively effective. (a) There is evidence that the presence of copper ions in water may be detrimental to galvanized iron. (b) There is possible evidence that color compounds may serve as inhibitors at Lindsay and Halifax (Chain Lake).

4. Aluminum is not resistant to waters containing copper salts or with a pH less than about 6-6.5.

5. For the few installations with copper pipe, the waters tested did not appear to be detrimental.

6. The quantity and the velocity of water flow is a factor that should be observed in greater detail in future studies of this type. This is particularly true for galvanized iron, and it is probable that the protective action of the zinc protection in the anomalous cases is dependent on the thickness of the zinc and the quantity of water passing over it. This was particularly noticeable for the LaVerne and the Lindsay (Visking) specimens.

References

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2. *J. Am. Wat. Works Assn.*, **28**, 1500 (1936); 34, 1667 (1942); **43**, 649 (1951).

3. *J. Am. Wat. Works Assn.*, 38, 182 (1946).

Inhibition of Corrosion of the Hypereutectic Aluminum-Silicon Alloys in Antifreeze Solutions*

By H. LEE CRAIG, JR. and PATRICK H. WOODS

Abstract

This paper presents results from laboratory corrosion tests of hypereutectic aluminum-silicon alloys under conditions related to those found in an automobile engine cooling system. Galvanic coupling to copper in the cooling system gives the greatest corrosion of the effects that were studied.

Laboratory tests of several inhibitors show that the corrosion of the hypereutectic aluminum-silicon alloys may be reduced to a negligible amount even when the metal is galvanically coupled to copper. These results are based on both stirring and pumping tests of inorganic and organic inhibitors added to single and double phase antifreeze solution. 5.8.1

Introduction

ALUMINUM CASTING alloys have been used in various automotive applications during the past 30 years. Many properties of aluminum, including light weight, ease in castability, high heat transfer, good machinability, availability, and low cost, combine to make this material a superior replacement for cast iron in engine blocks.[1] However, the property showing perhaps the greatest improvement over cast iron is the vastly superior corrosion resistance of aluminum, especially the aluminum-silicon alloys.

In the use of aluminum alloys for cast engine blocks, there are certain factors which could lead to serious corrosion problems:

1. The galvanic corrosion of aluminum in contact with heavy metals such as iron, copper, brass, and low melting solders which may be used in radiators, thermostats, and pumps.

2. The possible incompatibility of present inhibited antifreeze mixtures which could prove to be corrosion accelerators rather than inhibitors.

3. The tendency of aluminum to pit in aggressive waters which might be used in the cooling system.

4. The possibility of intergranular corrosion of improperly heat treated alloys containing large amounts of copper.

5. Crevice corrosion.

6. Corrosion of the cylinder wall and/or piston by the products of combustion of gasoline.

This report covers primarily points 1 and 2. Work is in progress in the other areas mentioned.

In order to rely on the background of general knowledge of the corrosion characteristics of aluminum, the literature has been reviewed and the metallurgy of these alloys is briefly presented.

Metallurgical Factors

Aluminum-silicon alloys containing up to 12 percent by weight of silicon have enjoyed use since about 1921, when an early distrust of silicon as an impurity was overcome through research and the introduction of "Siluman" alloys.[2] The corrosion characteristics of the hypoeutectic and eutectic alloys are well understood. For example, a wrought alloy of aluminum and 5 percent silicon is used for architectural purposes, not only because it develops a pleasing grey color upon anodizing but also because of the ability of thin sheets of this alloy to withstand deterioration over a long span of years.

Casting alloys employing silicon in amounts up to 12 percent, the eutectic point in the binary system, are among the most used alloys of aluminum. They are popular because they have a combination of moderate strength without heat treatment, ease in castability and corrosion resistance.

Figure 1 shows the aluminum end of the aluminum-silicon equilibrium diagram.[3] In order to obtain the wear resistance required for cylinder walls in an engine block, hypereutectic alloys containing from 15 to 25 percent silicon have been developed. Above the eutectic composition, the aluminum-silicon alloys are composed of eutectic composition interspersed with primary silicon. Refinement of the primary silicon is accomplished by a phosphorous addition.[4] Photomicrographs of hypoeutectic, eutectic, and refined hypereutectic compositions are shown in Figures 2, 3 and 4.

While the corrosion characteristics of this new class of alloys are expected to be very similar to those of the alloys containing 12 percent silicon and under, their proposed use in engine blocks requires an investigation of their specific properties, especially under environmental conditions related to a water cooled internal combustion engine.

Woods Craig

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Environmental Factors

Since waters generally used in the United States for automotive cooling systems are aggressive toward metals, it is a widespread practice to use inhibitors, either in combination with antifreeze solutions or by themselves.[5] The degradation products of some antifreeze solutions are corrosive to metals. Therefore, inhibitors necessarily are compounded with antifreeze formulations.[5] Automobiles with cast iron engine blocks will be used for many years along with newer aluminum engines, so it is desirable to have antifreeze solutions which are compatible with both metals. Within a given system, also, several different metals may exist, galvanically coupled or insulated, that will "see" the same antifreeze solution. For these reasons, efforts have been expended to determine the suitability of inhibitors and antifreeze solutions with the hypereutectic silicon alloys of aluminum.

Experimental Procedure

Materials

Six-inch tensile test bars rather than coupons of hypereutectic silicon alloys were used in testing. This was done because a one-half inch diameter round specimen is more representative of the sections found in an engine block than a 1″ x 2″ x ⅛″ coupon such as is specified in the ASTM glassware corrosion test.[7] Four cylinders were prepared from a single test bar, two retaining the original as cast surface and two machined down from one grip end to a one-half inch diameter by a simple lathe operation. The four cylinders were cut from the test bar and the flat ends smoothed on a belt grinder. The cylinder shaped test specimen was approximately one inch high, one-half inch in diameter with about one and one-half square inches of cylindrical surface.

In order to support the test specimens in the solution, a hole was drilled concentric with the long axis of the cylinder, through which a nylon rod was passed. A string of test specimens was placed on a rod, each separated from its neighbor by a polyethylene washer. The specimens were cleaned in acetone prior to immersion in the test solution.

Four hypereutectic alloys were cast with a nominal 15 weight percent silicon content and the following copper additions:

	Weight Percent Copper
Alloy A containing	0.35
Alloy B containing	0.55
Alloy C containing	1.07
Alloy D containing	5.01

*Submitted for publication January 18, 1960. A paper presented at the 16th Annual Conference, National Association of Corrosion Engineers, Dallas, Texas, March 14-18, 1960.

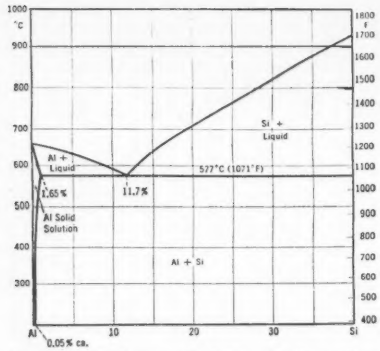

Figure 1—Aluminum end of the aluminum-silicon equilibrium diagram.

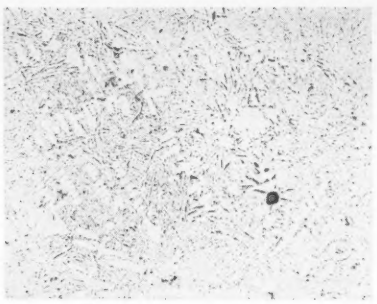

Figure 3—Al-12 percent Si alloy as cast. Structure consists mainly of Al-Si eutectic with localized areas showing both Si and Al as primary constituents. Not etched, approximately 50X.

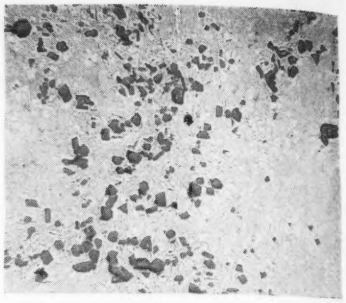

Figure 4—Al-20 percent Si alloy as cast. Primary Si on background of Al-Si eutectic. Refined with a phosphorus addition. Not etched, approximately 50X.

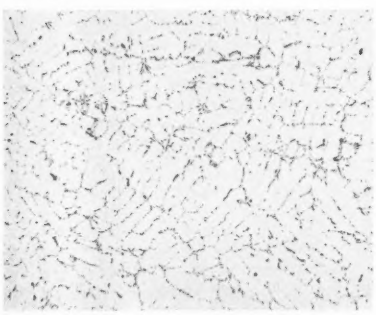

Figure 2—Al-4 percent Si alloy as cast. Eutectic Al-Si in the interstices of dendrites of primary Al. Not etched, approximately 50X.

Copper, of all the elements commonly found in aluminum alloys, generally has the greatest effect on the corrosion resistance of aluminum on a weight-percent basis.[5] Since copper may be desirable as an alloying element, the effects of copper additions were studied.

For the cast iron studies, grey cast iron typical of that found in present automobile engines was purchased in the form of one-half inch diameter rod.

Copper soft-temper type 1 tubing of greater than 99.9 percent purity was used for galvanic tests.

Test Details

Stirring Test. The rods were rotated by means of a stirrer at 230 rpm for time periods ranging from 3 to 36 days. An acidic type synthetic tap water was used with variations in glycol content. The composition of synthetic Altoona, Penn. water is given in Table 1. The ratio of the volume of solution to specimen surface area is 20 cc/sq. in. Tests were run at 160 F. Variations in each test condition were made to check the effect on corrosion rate. For the galvanically coupled samples, equal sized cylinders of copper were placed on the rod next to the aluminum cylinder.

Pumping Test. Another test was used involving a different apparatus but with the same general conditions. Test solutions in a stainless steel bucket were maintained at 160 F by immersion heaters. A pump was used to circulate the solution past strings of specimens suspended in a 2-inch diameter plastic tube, one of which was attached to the inlet and one to the outlet of the pump. This test is closer to the conditions found in an engine cooling system, but requires greater amounts of solution and more space than the stirring test. For this reason it is used as a confirming test for inhibitors passing the stirring test.

Sample Evaluation

After either exposure, samples were cleaned with a soft brush under tap water. Then they were dipped into concentrated nitric acid at room temperature, rinsed, placed into a 2 percent chromic-5 percent phosphoric acid solution for 10 minutes at 180 F, rinsed, dipped again in concentrated nitric acid at room temperature for three minutes, rinsed, and allowed to air dry. If examination of the specimen shows corrosion products still present, the procedure is repeated until none are detected.

Net weight losses of corroded specimens are calculated by subtracting blank weight losses determined on unexposed samples given the cleaning treatment from the gross weight loss of the corroded specimens.

At least duplicate specimens are run in each test. Milligrams per square decimeter per day (mdd) are calculated from the formula:

$$\frac{\text{Weight loss (milligrams)}}{\text{area (decimeters)} \times \text{exposure time (days)}}$$

Results and Discussion

Effect of Time, Temperature and Agitation

Weight losses are given in Table 2 for Alloys A, B, C and D in ethylene glycol and synthetic Altoona water (1:1 by volume) at room temperature with no stirring after 4.5 and 9 days and after 4.5, 9, and 36 days at 160 F with continuous stirring at 230 rpm. The data for continuous stirring of the alloys is plotted in Figure 5. After a brief induction period, the weight loss under these conditions is linear with respect to time. In order to eliminate the effect of the induction period the slope was measured in the calculation of these corrosion rates. Uniform corrosion rates are greater with the elevated temperature stirring test but the room temperature stagnant test develops pitting attack. Pit depths on these short term specimens are small; longer tests are in progress.

TABLE 1—Analysis of Synthetic Altoona, Penna. Tap Water*

Constituent	Concentration (Parts Per Million)
Silica	4.7
Iron	.07
Aluminum	1.4
Manganese	1.4
Calcium	14.2
Magnesium	4.2
Barium	.05
Strontium	.05
Sodium	2.8
Bicarbonate	.0
Sulfate	61.4
Chloride	4.4
Fluoride	.0
Nitrate	.0
Copper	.11
Cobalt	.08
Nickel	.03
pH	4.5

* This solution was prepared by dilution from stock solutions.

Effect of Galvanic Coupling

Corrosion rates (mdd) of Alloys A, B, C and D, freely corroding and galvanically coupled to cast iron and copper are given in Table 3. The samples coupled to copper show greater corrosion rates than those coupled to cast iron.

The effect of copper in the alloy on galvanic coupling to copper is shown in Figure 6. There is a pronounced minimum in the galvanically coupled rate curve in the vicinity of 1 percent copper. Alloy C also has the lowest weight loss when coupled to iron as well as to copper (see Table 3). As the copper content of the aluminum-silicon alloy is increased, the potential difference between the alloy and the coupled copper (Figure 7) becomes less and, therefore, the effect of galvanic coupling is diminished. Additions of copper to the aluminum in excess of 1 percent do not minimize coupling effects any further. Larger copper contents in aluminum alloys result in even greater corrosion for both coupled and freely corroding samples.

Corrosion rates for cast iron freely corroding and coupled to copper are also given in Table 3. Cast iron exhibits much greater corrosion rates than any of the aluminum alloys.

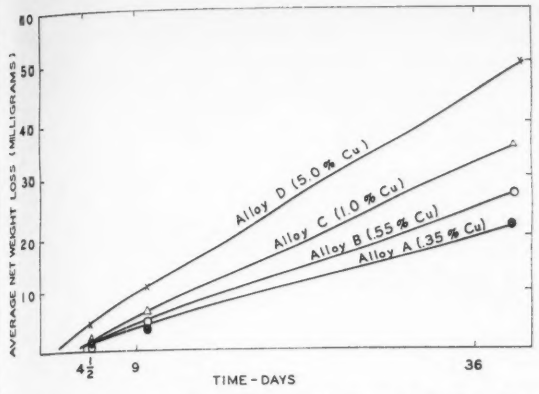

Figure 5—Corrosion rate of copper-bearing hypereutectic aluminum-silicon alloys in synthetic Altoona water and ethylene glycol (1:1) by volume.

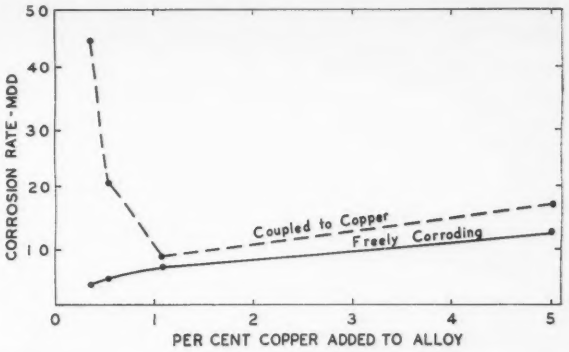

Figure 6—Effect of galvanic coupling to copper on the corrosion rate of copper-bearing hypereutectic aluminum-silicon alloys in synthetic Altoona water and ethylene glycol (1:1) by volume.

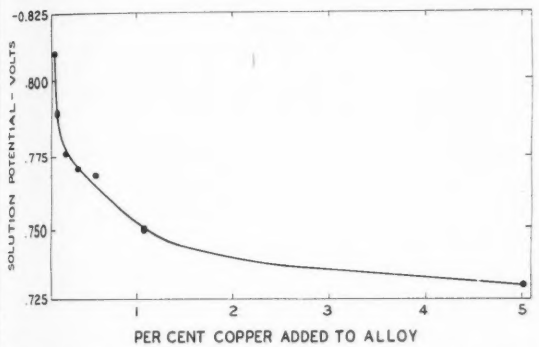

Figure 7—Solution potential of aluminum-silicon alloys as a function of copper content in the alloy. Measurements were made in 1N NaCl solution containing 0.3 percent hydrogen peroxide vs. a 0.1N calomel electrode.

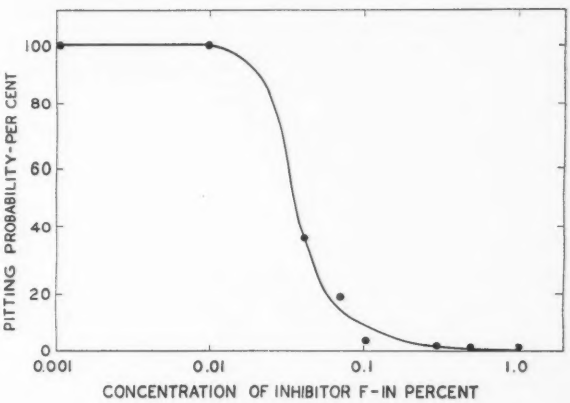

Figure 8—Pitting probability of 3003 aluminum alloy as a function of inhibitor F concentration in Richmond tap water.

Minor Test Effects

In all tests there was no significant difference between an "as cast" and a machined surface. Corrosion rates of Alloy C in synthetic Altoona water with ethylene glycol or methanol and a synthetic neutral hard water with ethylene glycol or methanol are given in Table 4. This latter water contains 200 ppm of bicarbonate ions as the calcium salt and 10 ppm of chloride ions as sodium chloride. Synthetic Altoona water is more aggressive than the synthetic neutral hard water and the methanol reduces the attack in both waters more effectively than ethylene glycol.

Corrosion rates of Alloy A are determined at stirring speeds of 230 rpm and 360 rpm. A stirring speed of 230 rpm corresponds to 28.7 feet per minute and 360 rpm corresponds to 45 feet per minute. An increase of stirring speed in this range decreases the weight loss from 27.3 mdd to 24.4 mdd for Alloy A when uncoupled but with a water to glycol ratio of 2 to 1 by volume.

Corrosion rates of Alloys A, B and C when galvanically coupled to copper at volume to area ratios of 20 ml/sq. in., 66.7 ml/sq. in. and 291 ml/sq. in, are given in Table 5. An increase in the volume to area ratio increases the corrosion of these alloys.

TABLE 2—Average Net Weight Losses of Test Alloys*

ALLOY	Weight Percent Copper	Time On Test (Days)	AVERAGE NET WEIGHT LOSS (Milligrams) Stagnant	Stirring
A	0.35	4.5	0.9	1.4
		9	1.1	3.4
		36	....	22.2
B	0.55	4.5	1.8	1.8
		9	1.7	4.4
		36	....	27.2
C	1.07	4.5	1.0	1.3
		9	0.9	6.0
		36	....	35.5
D	5.01	4.5	....	4.4
		9	....	10.7
		36	....	49.4

Blank weight losses due to cleaning procedure: Alloy A 1.2 mg; Alloy B 1.0 mg; Alloy C 1.0 mg; Alloy D 2.2 mg.

* For stagnant tests at room temperature (70 F) and for continuous stirring tests (230 rpm) at 160 F.

TABLE 3—Corrosion Rates for Coupled Metals*

MATERIAL	Percent Cu	CORROSION RATE (mdd) Freely Corroding	Coupled To Cast Iron	Coupled To Copper
Alloy A	0.35	3.9	4.9	44.5
B	0.55	5.0	5.2	20.3
C	1.07	6.9	0.9	8.6
D	5.01	12.5	....	16.5
Cast Iron	....	49.1	....	436.0

* Alloys A, B, C, and D freely corroding and galvanically coupled to cast iron and copper; cast iron freely corroding and coupled to copper in synthetic Altoona water and ethylene glycol (1:1 by volume).

TABLE 4—Corrosion Rate of Alloy C in Synthetic Waters Containing Ethylene Glycol or Methanol*

Solution	Corrosion Rate (mdd)
Synthetic Neutral Hard Water and Methanol (2:1)	3.2
Synthetic Neutral Hard Water and Ethylene Glycol (2:1)	4.2
Synthetic Altoona Water and Methanol (2:1)	8.1
Synthetic Altoona Water and Ethylene Glycol (2:1)	24.2

* Ratios given are on a volume basis.

TABLE 5—Corrosion Rates of Alloys A, B and C Coupled to Copper at Various Volume of Solution to Area of Sample Ratios

Material	Ratio of Volume Solution To Area of Sample		
	20 ml/ Sq. In.*	66.7 ml/ Sq. In.*	291 ml/ Sq. In.**
	Corrosion Rate (mdd)		
Alloy A	44.5	65.7	....
B	20.3	58.3	70
C	8.6	....	76.4

* Stirring Test.
** Pumping Test.

Inhibition of Corrosion

Initial screening results from stirring tests on Alloys B and C are given in Table 6. Two accelerators were noted (H and K). The very low initial pH of H probably accounts for its accelerating influence. Aluminum is stable in aqueous solutions because the oxide film is stable and capable of reforming when damaged. The broad pH range of this stability is from about 3.5 to 9, excluding situations where vigorous oxidizing agents or inhibitors are present. Outside these limits, the oxide film is appreciably more soluble, resulting in increased corrosion.

The final pH of K is not as high as A, and yet it is much more corrosive, showing that pH is not the only criterion for the corrosion of aluminum.

Pumping test results for Alloys B and C in uninhibited and inhibited Altoona water and ethylene glycol (1:1 by volume) at 160 F and galvanically coupled are shown in Table 7. B is a single phase antifreeze formulation supplied by a chemical company. Inhibitor F was chosen from the screening tests because it was more soluble than the other effective inhibitors in both ethylene glycol and water.

Pitting probability tests[9] with inhibitor F on 3003 wrought aluminum alloy have shown the inhibitor to be effective at as low as 0.1 percent concentration on this alloy (Figure 8). Pitting probability is defined as the number of samples with one or more pits divided by the total number of samples exposed. Tests in progress show that this inhibitor prevents pitting attack on the hypereutectic aluminum-silicon alloys under stagnant room temperature conditions. The inhibitor has also been on test six months in Alclad 3003 heat exchangers and has been performing well.[10]

TABLE 6—Inhibition Screening Tests on Aluminum-Silicon Alloys*

Inhibitor	Chemical Type	Concentration, Percent	pH		Corrosion Rate, mdd
			Before	After	
Blank		....	5.5	6.9	18.2
A	Tannin type with inorganic salts—single phase.	1.0	9.0	9.4	7.1
A	Tannin type with inorganic salts—single phase.	0.1	8.0	8.3	3.8
B	Inorganic salts—single phase	**	....	....	4.8
C	Inorganic salts + soluble oils—double phase.	**	7.3	7.1	3.2
D	Organic phosphorous compound—single phase.	1.0	4.8	5.1	1.5
D	Organic phosphorous compound—single phase.	0.1	5.3	6.1	3.0
E	Organic phosphorous compound—single phase.	1.0	7.8	6.7	0.6
E	Organic phosphorous compound—single phase.	0.1	6.9	6.5	3.6
F	Organic phosphorous compound—single phase.	1.0	8.8	6.3	0.8
F	Organic phosphorous compound—single phase.	0.1	7.0	6.3	0.9
G	Organic phosphorous compound—single phase.	1.0	2.2	6.3	1.5
H	Organic phosphorous compound—single phase.	1.0	1.5	5.0	25.8
I	Rice oil—double phase	1.0	6.5	5.4	7.1
J	Rice oil—double phase	1.0	6.4	6.1	0.8
K	Amine salt of fatty acid—double phase.	1.0	6.0	9.0	183.3
L	Rice oil—double phase	1.0	6.5	7.8	1.1
M	Amine salt of fatty acid—double phase.	1.0	9.3	8.4	2.3
N	Amine salt of fatty acid—double phase.	1.0	7.7	8.1	3.2

Note: Inhibitors I through N and B were tested with Alloy C; all others with Alloy B.
* Solution is Altoona water and ethylene glycol or antifreeze formulation (1:1). Samples galvanically coupled to copper.
** Proprietary inhibited antifreeze formulation.

TABLE 7—Results of Simulated Engine Cooling System Test of Selected Inhibitors for Aluminum-Silicon Alloys

	CORROSION RATE—mdd		Percent Inhibition
	Uninhibited	Inhibited	
Inhibitor F (Alloy B)	70	3	95.9
Inhibitor B (Alloy C)	76	19	75.0

Note: Pumping test for 3 days with samples galvanically coupled to copper. 0.5 percent inhibitor F was added to a 1:1 mixture of synthetic Altoona water and ethylene glycol at 160 F. Inhibitor B was added as an antifreeze formulation to synthetic Altoona water (1:1 by volume).

Conclusions

1. Several inhibitors are effective in reducing the corrosion of galvanically coupled hypereutectic aluminum-silicon alloys. For example, inhibitor F decreases the corrosion from approximately 70 mdd to about 3 mdd in simulated engine cooling system tests.

2. Tests have been run for various times up to 36 days and weight losses have increased with increasing time at a steady rate, under the conditions of continuous agitation and elevated temperature.

3. Pitting of aluminum has been found only in stagnant room temperature tests, but is prevented by the use of an inhibitor such as inhibitor F.

4. Coupling to either copper or cast iron increases the corrosion of the hypereutectic aluminum-silicon alloys.

5. Aluminum resists corrosion better than cast iron. Corrosion rates on aluminum have ranged up to 76.4 mdd for time periods up to 36 days, whereas cast iron corroded at a rate of 436 mdd in seven days tests.

6. Under the conditions of constant stirring at 160 F, no difference in corrosion rate is detected between "as cast" and machined surfaces. An acid, hard tap water, was more corrosive than a neutral, hard tap water. Ethylene glycol is less effective in reducing corrosion than methyl alcohol in an uninhibited antifreeze mixture. An increase in the ratio of volume of solution to specimen surface area increases the corrosion rate whereas a variation in the stirring speed affected the corrosion rate only slightly.

Acknowledgments

The contributions of the following personnel of Metallurgical Research Laboratories are gratefully ackowledged: G. E. Stein, G. P. Koch, J. W. Carson, R. S. Mapes, J. R. Scott and H. B. Romans.

Inhibitors were supplied by Armour Chemical Company, Comet Rice Mills, Dow Chemical Company, and Virginia-Carolina Chemical Corporation.

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Concentration Cells and Aqueous Corrosion*

By EDWARD SCHASCHL and G. A. MARSH

Abstract

This paper describes improved technique for continuous recording of maximum current output of concentration cells and for obtaining corrosion rates of cell electrodes over short periods. Generally, where a dissolved oxygen concentration cell competes with another, the dissolved oxygen cell takes precedence and is the current determinating cell. Rust film on steel increases activity of local or physically separated dissolved oxygen cells. Cell action can be calculated by an equation developed from Fick's law of diffusion. 3.6.2

Introduction

THE ELECTROCHEMICAL nature of the aqueous corrosion of steel can be demonstrated very convincingly by the simple dissolved oxygen concentration cell shown in Figure 1. The aerated zone of the cell forms the cathodic compartment, while the deaerated zone forms the anodic compartment. Typical reactions in these compartments are:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad \text{(cathodic)}$$

$$Fe \rightarrow Fe^{++} + 2e \quad \text{(anodic)}$$

While the present discussion will deal with several forms of concentration cells, the cells involving dissolved oxygen are of greatest interest both from historical and mechanistic points of view.

This paper will include the description of a new technique in which cell currents and the corresponding corrosion rates are measured on the same cell electrodes in a split cell. Also, in this new technique, the cell currents are measured under conditions of zero external resistance by means of a recording zero resistance ammeter.

The experimental work shows that other concentration cells are feeble compared to the dissolved oxygen cell and that, in a general case, where any competition takes place the dissolved oxygen cell takes precedence. The effect of rust scale on suppressing further corrosion is dealt with on the basis of cell action. The behavior of a cell when an inhibitor is placed separately in the compartments is discussed briefly.

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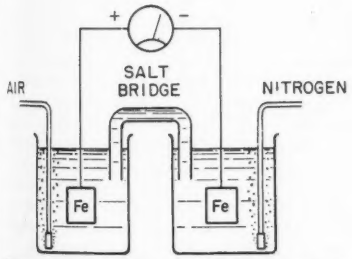

Figure 1—Simple dissolved oxygen concentration cell.

Marsh Schaschl

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Early Work

Lynes, in his comprehensive review[1] pointed out that the dissolved oxygen concentration cell had been observed by a number of workers in the 19th Century. The action of the cell was first explained by Evans[2] in 1923.

Subsequent work by Evans[3] and by Herzog[4] revealed interesting properties of this cell. A comparison of current output with weight loss of the anode showed that Faraday's law was obeyed, thus demonstrating the electrochemical nature of corrosion. It was discovered that diffusion of oxygen controls the output of the cell; the greater the oxygen concentration in the cathodic region (for a given concentration in the anodic region) or the greater the cathodic area, the greater the cell current.

Tödt[5] was one of the first to utilize the phenomenon of oxygen reduction at a cathode; he measured the current output of simple cells to determine the dissolved oxygen content of water.

Many workers have obtained open circuit potential and polarizing characteristics, (i.e., change in potential with passage of current). But closed circuit current, especially with zero resistance in the external circuit, is of special interest because this is the current that is related to the anodic dissolution rate.

In previous work, the zero resistance ammeter was not employed insofar as is known, so that maximum current output could be obtained only indirectly from polarization data. Also, there has been no convenient way of measuring corrosion along with cell current. Despite these limitations, the numerous studies of oxygen concentration cells have provided important background for what is probably the most common system in the field of corrosion.

The open circuit electrode potential of steel is 0.3 to 0.7 volt more negative

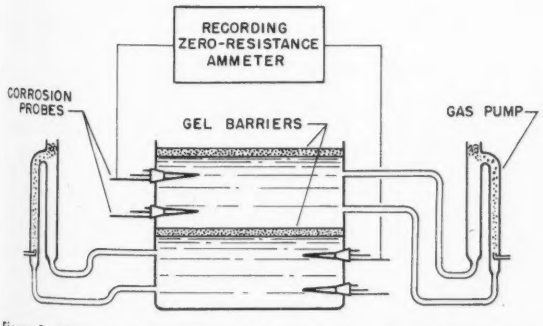

Figure 2—Diagram of the split cell. The gel barriers separate the cell into zones which are electrolytically connected. The corrosion probes serve both as corrosion sensing devices and as electrodes of the cell.

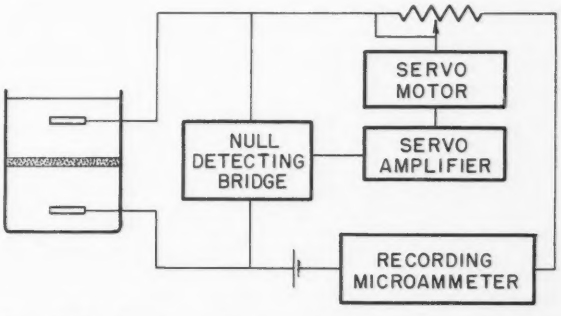

Figure 3—Recording zero resistance ammeter. This device eliminates the IR drop normally associated with measurement of current.

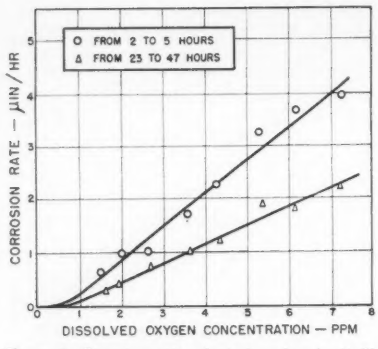

Figure 4—Corrosion rate of steel probes in NaCl solutions (fluid velocity 1 in/sec).

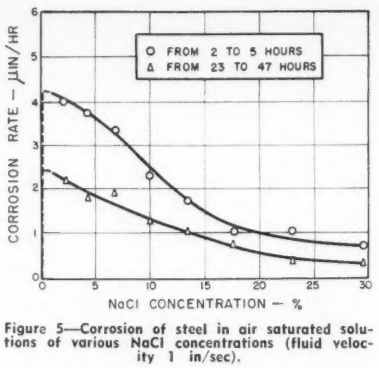

Figure 5—Corrosion of steel in air saturated solutions of various NaCl concentrations (fluid velocity 1 in/sec).

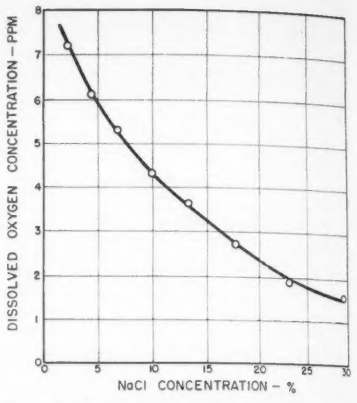

Figure 6—Dissolved oxygen concentration in air saturated NaCl solutions at 77F.

TABLE 1—Characteristics of a Typical Simple Dissolved Oxygen Concentration Cell

Area	pH	NaCl, Conc., %	Dissolved Oxygen Conc., ppm	"Blank" Rate, i.e. Corrosion Rate of Steel in Absence of Cell Action, μ in./hr.	Corrosion Rate of Steel When Connected in Cell μ in./hr.	Cell Current Density ma/ft²	Corrosion Rate, in Anodic Zone Calc'd from Cell Current, μ in./hr.
Anodic Zone...	7.0	3	0	0.12	5.2	90	5.1
Cathodic Zone...	7.0	3	6.5	2.9	0.0	90	..

in deaerated neutral solutions than it is in air saturated solutions. This potential constitutes the driving force for the common rusting of steel. The maximum current that can be obtained from an oxygen concentration cell depends primarily on the rate at which oxygen is brought to the cathodic surface. The ohmic resistance in the electrolytic path is usually a secondary factor. At high corrosion rates some anodic polarization may occur but this is negligible in the ordinary case.

Experimental Setup

Figure 2 shows in schematic form the equipment used in the split cell technique. A vertical series of holes was made in the side of a battery jar of 16 qt. capacity. These holes permitted access to various depths of liquid in the jar. A tight-fitting agar gel barrier of 0.3 inch thickness was "cast" in place in such a way that the upper half of the cell was isolated from the lower half. This gel barrier was retained on filter paper which in turn was supported by a Lucite disk. The disk was perforated with numerous holes 0.4 inch in diameter. The gel barrier, while restricting the transfer of oxygen and dissolved salts from one zone to the other, offered only slight resistance to the passage of ionic current. Another barrier at the top of the cell excluded atmospheric oxygen.

The jet "bubblers" or gas pumps shown in Figure 2 were especially designed to permit saturation of each zone separately with a gas, to effect aeration or deaeration. As these bubblers were open to the atmosphere at the top they provided a convenient access to the separate zones for such purposes as determining pH and conductivity.

Besides providing gas saturation, the bubblers introduced a certain amount of agitation into the zones of the cell. It was necessary to maintain agitation constant from one run to another since cell current was very sensitive to agitation. To this end the gas flowing to each bubbler was adjusted or reset using a sensitive flowmeter. The flow through each bubbler was determined initially by adjusting each pressure until the degree of agitation was about the same in both zones, as evidenced by zero current flow in an oxygen concentration cell in which all constituents other than agitation were equally matched.

Two or more steel electrical resistance corrosion test probes could be inserted into each of the two isolated zones of the cell. These probes were constructed in the same manner as described in a previous publication from this laboratory. They were mounted on rubber stoppers (Type A, Figure 3 in Reference 6). The initial thickness of the probes was 0.005 inch.

Surface preparation of probes is an important consideration for short term tests. In the case of the present work, preparation consisted of an etch in 6N HCl in which 1 percent ferric chloride was dissolved. The probes were etched 10 seconds at room temperature, then washed in water and acetone, dried and stored temporarily in a desiccator until the cell was ready to be filled.

It is apparent that the probes can be used for *in situ* corrosion measurements as described in Reference 6. In the cell experiments described here, the probes served as cell electrodes as well. This permitted direct observation of the corrosion rate of steel while the probe was acting as a cell anode or a cell cathode in a concentration cell. (The terms cell anode and cell cathode are used to indicate that the anodic or cathodic behavior is caused by concentration cell action. There would be no corrosion at a true cathode, but there might be corrosion of a *cell cathode* as a result of local action.) The probes also permitted a detailed study of the relationship between dissolved oxygen concentration, local action, and cell action.

While a manual zero resistance ammeter could have been used for some of the experiments, a recording apparatus proved to be essential for most of the runs. The recording zero resistance ammeter used was designed by L. E. Ellison of the Pure Oil Research Center and is shown in block diagram form in Figure 3. Any voltage appearing across the null detecting bridge causes an unbalance in the input to the servo amplifier. The servo then rotates the rheostat in the direction needed to increase or decrease the applied current and restore zero voltage across the bridge. Since the potential between electrodes is maintained at zero volts, the electrodes are essentially short-circuited. The current flow in the rheostat circuit is the same current that would flow between the electrodes if they actually were short circuited. This current is applied to a continuous strip chart recorder which has a 0-1 milliampere range.

In most of the systems studied, the zero resistance current varied over wide limits during the course of the experiment. The recording zero resistance ammeter accurately followed the current and permitted the experiments to run unattended.

Units

Some of the quantities used and developed in this investigation are commonly expressed in metric units, but others, notably corrosion rates and current densities, are most commonly reported in English units. For the sake of consistency, English units will be used throughout.

Corrosion rates expressed as microinches penetration per hour can be converted to ipy by multiplying by 0.00875. A corrosion rate of one microinch per hour when expressed as anodic current density is equivalent to 17.8 ma/sq. ft.

Background Data

In order to illustrate the behavior of the probes used in this study, some data are included here on the rate of corrosion under various conditions. The rates

are given in units of microinches per hour.

A clean acid-dipped probe immersed in a dilute aerated salt solution (not connected in a concentration cell) corrodes at approximately twice as high a rate during the first five hours as it does after 25 hours. This effect, illustrated in Figures 4 and 5, is believed to be caused by the gradual build-up of rust scale on the probe. Figure 4 also illustrates the effect of dissolved oxygen on this "blank" rate (i.e., probe unconnected in a cell).

Figure 5 illustrates the corrosion of steel in air-saturated sodium chloride solutions. Because sodium chloride content affects the dissolution of oxygen, this figure is explained in part by the effect of dissolved oxygen on corrosion rate. Figure 6 is a plot showing dissolved oxygen concentration (by Winkler's method) as a function of NaCl concentration in saturated solutions. A similar plot was obtained by Hache[7] but his data were consistently lower in dissolved oxygen (by about 0.5 ppm) than were the authors'.

The data of Figures 4 and 5 were for a condition of fairly uniform agitation, about 1 inch per second liquid velocity. Small variations in the degree of agitation of aerated solutions had a pronounced effect on corrosion rate. The importance of agitation control in cell work cannot be over-emphasized.

Studies of a Simple Concentration Cell (One Concentration Variable)

In a typical simple dissolved oxygen concentration cell, such as one finds in a crevice, an air-saturated solution might contact the cathodic area of the steel surface, and an air-free solution might contact the anodic area. Except for the dissolved oxygen content, both solutions would have the same composition. Such a case was studied in the split cell by maintaining an air-saturated and an air-free solution respectively in the two zones. The areas of the anodic and cathodic surfaces were equal. The recording zero resistance ammeter was connected between two probes, one in each zone of the cell. Conductivity and pH were maintained constant in both zones.

Agitation of the solution in the anodic zone had no effect on cell current, as one would expect from a system under cathodic control. Agitation of the solution in the cathodic zone, however, affected current output of the cell. Minor variations in agitation (caused by thermal currents and moment-to-moment fluctuations of agitation created by the bubblers) caused a fairly rapid drifting of cell current up and down, about 5 percent above and 5 percent below the average value. Over a long time period, the average current remained constant, so long as the oxygen difference and agitation were held constant. Typical conditions for this type of cell are listed in Table 1.

It will be noted from Table 1 that unconnected ("blank") probes in the anodic zone corroded at a feeble rate while blank probes in the cathodic zone corroded at a moderate rate. When the probes were connected to form a cell, the corrosion rates were changed drastically (i.e., the anodic probe increased in rate from 0.12 to 5.2 μ in./hr), while the cathodic probe decreased in rate from 2.9 to 0 μ in./hr. The zero resistance cell current density was 90 ma/ft^2 on both the anode and cathode.

The current density of 90 ma/ft^2 was sufficient to cathodically protect the cathodic probe; hence the corrosion rate of the probe in the cathodic zone of the cell became zero. When the measured cell current was converted to the corresponding corrosion rate, by means of the constant for Faraday's law, the rate so obtained was close to that actually measured on the anodic probe. This constitutes another simple incontrovertible demonstration of the electrochemical nature of aqueous corrosion.

In other experiments, cell action was insufficient to cathodically protect the cathode, (viz. the connected probe in the cathodic zone). Under these conditions the cathode corroded with the formation of a rust layer. As this rusting proceeded, it hindered the diffusion of dissolved oxygen to the cathode surface. Drifting of cell current eventually stopped as the cathode became less and less sensitive to agitation. Cell current itself gradually declined.

Many runs were made with simple dissolved oxygen concentration cells in order to study this interesting effect of scale formation.

Effect of Concentrations in Complex O_2-NaCl Cells at Constant pH

Complex concentration cells are those having more than one variable component. Complex cells with dissolved oxygen as one of the components are especially interesting, since they are the most common in nature. For example, a complex cell having as variables (1) dissolved oxygen, and (2) dissolved solids, occurs in some estuaries where steel piles penetrate water varying from fresh water at the surface to sea water at the bottom. In such cases commonly there is more dissolved oxygen near the surface than near the bottom of the water.

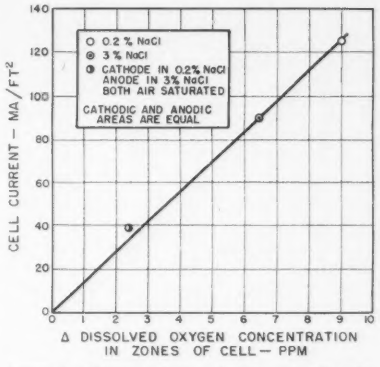

Figure 7—Cell current as a function of delta dissolved oxygen concentration.

A number of experiments were carried out in the split cell, with results shown in Figure 7. The three data points on Figure 7 are not merely the results of three experiments. Each of the points represents initial conditions for a particular experimental cell:

Cell 1. Both zones contained 0.2 percent NaCl. The cathodic zone was air-saturated; the anodic zone was deaerated. The Δ dissolved oxygen concentration was 9 ppm.

Cell 2. Both zones contained 3 percent NaCl; the cathodic zone was air-saturated, anodic zone deaerated, Δ dissolved oxygen concentration 6.5 ppm.

Cell 3. The cathodic zone contained 0.2 percent NaCl; the anodic zone contained 3 percent NaCl. Both zones were air-saturated, but owing to the different solubility of oxygen in the two NaCl solutions the Δ dissolved oxygen concentration was 2.5 ppm.

These cells yielded particular values of cell current as shown on Figure 7. The cell currents were then continuously recorded while the dissolved oxygen in the cathodic zones was gradually removed to the condition of complete deaeration. Periodically, the dissolved oxygen con-

TABLE 2—Characteristics of a Complex Cell*

Zone	pH	NaCl Conc., %	Dissolved Oxygen Conc., ppm	Time After Start of Test, hrs.	Cell Current Density, ma/ft^2	Corrosion Rate of Steel, μ in./hr.		
						In Absence of Cell Action ("Blank")	When Connected in Cell	Calc'd. from Cell Current
Anodic	7.0	3.0	6.5	0	50	3.4	7.0	2.8
				5	114	3.4	9.5	6.4
Cathodic	7.0	0.2	9.0	0	...	4.3	3.2	..
				5	...	4.3	0.6	..

* This table illustrates that cell action in a salt concentration cell results from different oxygen solubilities in the zones of the cell. After 5 hours sufficient corrosion products have been deposited at the anode to shield it from what oxygen is available: the corrosion rate therefore increases.

TABLE 3—Cathodic Film Thickness X_c Under Mildly Agitated Conditions (1 inch/sec)*

Metal Loss at Cathode by Previous Corrosion, μ in.	Cell Current I, μa	Current Density at Cathode ma/ft^2	Δ Dissolved Oxygen Conc. (ΔB), ppm	Cathodic film thickness X_c (from Eq. 6) in.
0	600	120	9.0	0.0065
0	760	152	9.0	0.0052
3	580	116	6.5	0.0049
10	670	134	9.0	0.0059
11	440	88	6.5	0.0065
11	460	92	6.5	0.0062
18	570	114	9.0	0.0069
20	580	116	9.0	0.0068
20	420	84	6.5	0.0068

* In this table cathodic film thicknesses are calculated from Equation 6 for various runs in which the cathode was allowed to corrode to a given metal loss prior to being connected as a cell.

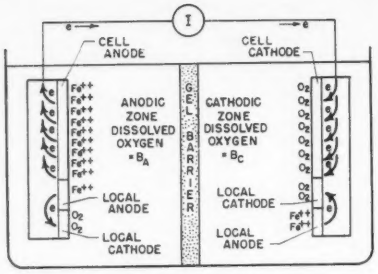

Figure 8—Schematic diagram showing local action and cell action in split concentration cell. Ionic current through electrolyte is not shown. See text for discussion.

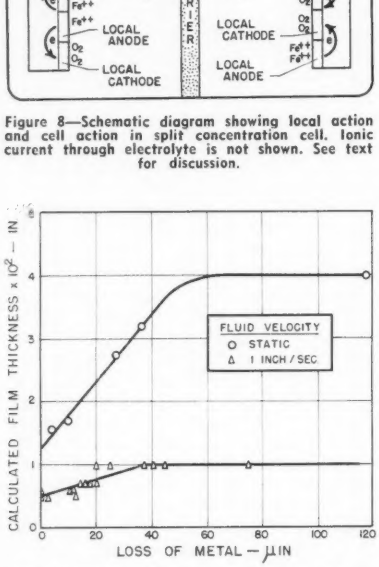

Figure 9—Relationship between thickness of diffusion film, initial corrosion and agitation.

centrations in the cathodic zones were measured. In this way three essentially continuous plots of cell current vs Δ dissolved oxygen concentration were obtained. The three curves turned out to fall identically on top of each other, yielding the single straight line of Figure 7.

In other experiments, NaCl concentration was varied by increments, and cell current and Δ dissolved oxygen concentration were plotted. The data fell again on the line of Figure 7 within experimental error, regardless of the NaCl concentration in the two zones of the cell. If one zone contained a higher dissolved oxygen concentration than the other zone, the higher oxygen zone was always cathodic, even when it contained a higher NaCl concentration than the other zone. The cell current was independent of NaCl concentration provided there was sufficient conductivity in each zone to prevent resistance control.

Thus difference in oxygen concentration alone is responsible for cell current in this type of complex cell. This result is contrary to the frequently made statement that in a salt concentration cell the more concentrated zone is anodic.

Effect of Corrosion Products or Rust Scale on Concentration Cell Action

From the foregoing observation, one should expect cell action from steel in *air saturated* solutions of 0.2 percent NaCl and 3 percent NaCl, because these solutions contain different amounts of oxygen when air saturated. (The difference amounts to 2.5 ppm.) This cell was set up using solutions of pH 7.0*. The cell current varied with time as shown in Table 2.

In the cell described in Table 2, (the cell having a high degree of aeration at the cathodic zone), some local action occurred at the cathode as evidenced by a low but definite corrosion rate. This is of interest in view of the fact that the current density supplied to the cathode was over 100 ma/ft².

The difference in oxygen solubility, 2.5 ppm, caused the cell to function initially. Steel in the 3 percent NaCl solution became anodic not because of the higher salt concentration but rather because of the lower dissolved oxygen concentration. As corrosion proceeded in the anodic zone, the anodic surface became coated with insoluble corrosion products which decreased the availability of oxygen to the surface of the anode. This in turn decreased local action and increased cell current, as shown in Table 2. A vigorous cell resulted from rather mild initial conditions.

In a general case, as corrosion proceeds in either zone, the steel becomes covered with corrosion products or scale if dissolved oxygen is present. At first the scale is a porous film of hydrous ferric oxide. As the film builds up in thickness, the film decreases the availability of oxygen at the surface. If this occurs at the anode, it causes the anodic reaction to proceed more vigorously than before. Finally a maximum cell action is reached when ferrous ions are being formed faster than the equivalent amount of dissolved oxygen can diffuse to the the anodic surface. Under this condition the anode reacts as if it is completely deaerated in spite of the fact that the bulk solution surrounding the anode continues to be air-saturated throughout the experiment.

This situation is dependent upon the oxygen content in the bulk solution of the anodic zone. If the oxygen content is initially zero, no rust scale can form and there will be no change in cell current with time. If the oxygen content is appreciable, the cell current will be low initially and will gradually increase to the value that would be observed if the anodic zone was deaerated.

The effect being described, a "snowballing" of cell current, can also originate in a split cell where conditions in both compartments are practically identical. It is well known that two similar pieces of steel will usually differ slightly in electrode potential; if such specimens are used as cell electrodes the cell current is feeble at first. The current gradually builds up to the maximum that would be observed in an aerated-deaerated cell.

Local action at the cathode results in the deposition of a hydrous ferric oxide film on the cathode, just as local action at the anode results in a film on the anode. It has just been seen that this film at the anode causes an increase in cell current. But as cell current increases, local action at the cathode decreases. Therefore, while any film at the anode gradually increases in thickness, the corresponding film at the cathode does not increase but remains permeable, eventually sloughing off the surface.

One condition needed to bring about the growth or retarding of films as described in the preceding paragraphs is low resistances in the cell. If the resistances are too high, cell action may not be vigorous enough to make itself apparent by affecting film growth.

Local Cell Action and Pitting, Theoretical Analysis

The foregoing paragraphs suggest the following qualitative analysis of pitting corrosion. If a polished steel surface is exposed to aerated distilled water the initial corrosion rate is known to be very low (cf Figure 5). Anodic and cathodic areas are present on the surface, but the resistance of the electrolytic paths between these areas is too high to permit more than a very feeble flow of ionic current. The local cells are under resistance control.

After a period of time, sufficient corrosion will have occured so that corrosion products begin to amass over the anodic areas. In so doing, these corrosion products increase the driving force for local cell action; the anodes soon become oxygen-free. Corrosion can proceed more vigorously, though still controlled by the high resistance of the electrolyte. At this stage definite pits develop on the polished surface.

Now corrosion products may accumulate in an amount sufficient to cover partially the cathodic area. At this point ionic current can flow through the film of corrosion products; the corrosion rate increases to a higher order of magnitude, probably under mixed resistance and diffusion control. The anodic areas spread under the film. Finally the cathodic areas may become covered with the corrosion products; the corrosion rate, being still under mixed control, remains fairly constant so long as a supply of oxygen is available.

The effect of agitation or velocity should therefore have a very pronounced effect on pitting. The agitation, if sufficient to remove the scale from cathodic areas, would increase their efficiency while if agitation is insufficient to remove this scale the corrosion process would become throttled as described above.

Thus, corrosion of polished steel in aerated distilled water initially takes the form of isolated pitting; the pitting rate gradually increases; finally the rate levels off and attack becomes more uniform as the anodic areas spread out under the blanketing corrosion products.

Cell Current as a Diffusion Phenomenon

The potentials responsible for cell current originate at the anodic and cathodic surfaces. In particular, the potential of the cathodic surface varies with the rate at which dissolved oxygen reaches this surface; hence cell current itself depends

* The pH was adjusted at brief intervals by means of small additions of NaOH or HCl. Buffers were not used because it was found that the citrate, phosphate, etc. used in buffers affected cell action, usually by inhibiting it.

TABLE 4—Calculation of Anodic Film Thickness X_a Under Mildly Agitated Conditions (1 in./sec)

Metal Loss at Cathode by Previous Corrosion, μ in.	Cathodic Film Thickness X_c from Figure 9, in.	Local Action L_c from "Blank" Rate, ma/ft²	Cell Current I, ma/ft²	Diff. in Dissolved Oxygen in Zones of Cell △B, ppm	Local Action L_a from "Blank" Corrosion Rate, ma/ft²	Metal Loss at Anode by Previous Corrosion, μ in.	Anodic Film Thickness X_a from Eq. 9, in.
3	0.0053	24	110	2.5	48	38	0.0101
7	0.0056	36	106	2.5	50	40	0.0098
8	0.0057	107	12	2.5	89	12	0.0052
9	0.0058	55	36	0	55	20	0.0096
14	0.0062	11	118	2.5	60	75	0.0098
14	0.0062	36	110	2.5	71	45	0.0098
16	0.0064	89	16	0	98	15	0.0069
17	0.0065	107	16	0	116	16	0.0069
22	0.0069	89	18	2.5	53	24	0.0098

upon this rate. The effect of rust scale on cell action can be looked upon as a special case of throttling of the diffusion of oxygen at the reacting surface of the cathodic metal.

Figure 8 may aid in analyzing the effects of the various factors on the overall cell. Utilizing Fick's law of diffusion, cell action at the cathodic surface may be represented as

$$kR_c = L_c + I = \frac{D(B_c - S_c)}{X_c} \quad (1)$$

and at the anodic surface

$$kR_a = L_a = \frac{D(B_a - S_a)}{X_a} \quad (2)$$

where:

R_a and R_c = the diffusion rates of dissolved oxygen at anode and cathode reacting surfaces, respectively;

D = the diffusion coefficient for dissolved oxygen,*

B_a and B_c = the concentration of dissolved oxygen in the bulk solutions,

S_a and S_c = the concentrations of dissolved oxygen at the reacting surfaces,

X_a and X_c = thickness of the film across which diffusion must occur. X_a and X_c may include scale as well as static liquid layer.

L_a and L_c = local action currents.

I = the measured cell current;

k = a unit conversion factor

R_c, the rate of diffusion of dissolved oxygen across the static liquid and scale layer adjacent to the reacting surface of the cathode, is the sum of two processes, the first of which is cell action as measured by the zero resistance cell current I in ma/ft² of cathode area. Cell action results in consumption of electrons at the cathode by the process:

$$O_2 + 2H_2O + 4e \rightarrow 4\,OH^-$$

Hence I, the cell current, is a direct measure of the part of R_c responsible for cell action.

The second component of R_c is local action at the cathode, L_c, expressed as ma/ft². In local action, a part of the surface of the steel in the cathodic zone of the cell is anodic. In corroding, this local action anodic area supplies cathodic areas nearby with electrons. Hence the total flow of electrons at the cathodic surface is the sum of those supplied by local action and by cell action. The rate of diffusion of dissolved oxygen at the cathode, R_c, depends upon this total current flow, so that R_c is proportional to the sum of cell action I and local action L_c at the cathode.

R_a is the corresponding rate of diffusion of dissolved oxygen at the anodic surface (in the anodic zone of the split cell, Figure 8). This rate is responsible for the local action at the anode. In the absence of dissolved oxygen, the entire surface of metal in the anodic zone would corrode and in so doing would contribute electrons to the cathodic zone by cell action; there would be no local action at the anodic surface. It will be noted that dissolved oxygen at the anode does not contribute to cell current.

If dissolved oxygen is available at the anodic surface, however, it can be reduced by electrons from adjacent areas. This local action process results in the removal or reaction of the dissolved oxygen and in the flow of local action current L_a. Hence L_a is proportional to R_a.

The concentration of dissolved oxygen can be much different at the reacting surfaces than in the bulk solution, but under steady state zero external resistance conditions the concentration of dissolved oxygen at both reacting surfaces must be equal. This is so because the electrode potentials must be practically equal when the cell is short-circuited; so long as the concentrations of oxygen at the surfaces are different the potentials will be different.

From this discussion it is apparent that $S_a = S_c = S$, where S is the concentration of dissolved oxygen at the reacting surfaces.

$$L_c + I = D\frac{(B_c - S)}{X_c} \quad (3)$$

$$L_a = D\frac{(B_a - S)}{X_a} \quad (4)$$

Since the term DS is common to both equations, substitution can be made and the resulting equation can be solved for I:

$$I = \frac{D\,(B_c - B_a) + L_a X_a - L_c X_c}{X_c} \quad (5)$$

The term $B_c - B_a$ is the difference in bulk dissolved oxygen concentration, △B, between the two zones of the cell. From this

$$I = \frac{D\,\triangle B}{X_c} - \frac{L_c X_c - L_a X_a}{X_c} \quad (6)$$

Equation 6 gives cell current in terms of its component factors. This equation can be used to determine both the cathodic and anodic film thicknesses from experimental data.

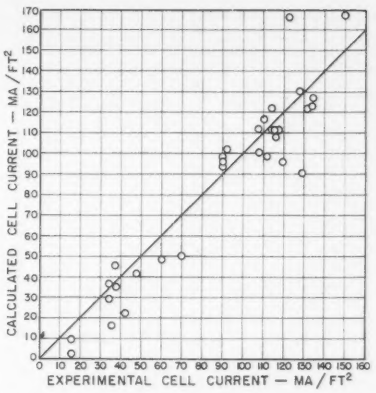

Figure 10—Comparison of experimental values of cell current with those calculated from Equation 6.

Calculation of X_c, Cathodic Film Thickness

Local action at the anode (L_a) is zero when there is no dissolved oxygen at the anodic compartment of the split cell ($B_a = O$). Local action at the cathode (L_c) is zero when the cell current is sufficiently high to cathodically protect the cathodic surface. With both L_a and L_c equal to zero, equation 6 becomes

$$I = \frac{D\,B_c}{X_c} \quad (7)$$

from which the diffusion film thickness X_c at the reacting cathodic surfaces can be calculated from measured quantities. Table 3 lists the results of typical experiments. The values of X_c were calculated taking the diffusion constant $D = 3.03 \times 10^{-6}$ in²/sec. It will be noted that Table 3 is for slightly agitated conditions. Under static conditions, X_c proved to be much greater, as one would expect.

Effect of Previous Corrosion on X_c

Figure 9, which is a plot of film thickness against metal loss at the cathode, shows how rust affects the cathodic film. In order to obtain this relationship, the cathodic probes were initially disconnected from the split cell, so that they corroded in the highly aerated solution in the cathodic zone. As indicated in Table 3, corrosion was allowed to proceed to varying extents in different experiments; then the cathodic probe was connected into the cell circuit and the cell current was measured.

The thickness of the cathodic diffusion film X_c reached a constant value after corrosion had removed 40 or 50 microinches. From this point on, the film thickness depended only on agitation. Under

* As a simplifying assumption, D is taken as the diffusion coefficient for oxygen dissolved in water and is considered to be the same for the films of both electrodes.

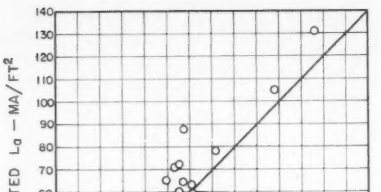

Figure 11—Comparison of L_a calculated from Equation 10 with experimental values.

static conditions the film was of macroscopic thickness, but slight agitation decreased this drastically; and in the case of violent agitation the thickness probably became vanishingly small. This thickness, together with the difference in bulk dissolved oxygen concentration, determines the cathodic current density when no local action occurs at the anode.

Local Action at the Cathode

The condition where no local action occurs at the anode is met in a practical case where the anodic zone is completely deaerated. However, local action at the cathode will proceed so long as electronic current from the anode is insufficient to cathodically protect the cathode.

From Equation 6 and Equation 7, L_c, local action at the cathode, may be found as

$$L_c = \frac{D \triangle B}{X_c} - I. \qquad (8)$$

In other words, L_c can be obtained conveniently in any run where L_a is zero. L_c is expressed in terms of corrosion current density, ma/ft^2.

Local Action at the Anode

Local action at the anode, as a first approximation, is equal to the "blank" rate of corrosion of unconnected probes in the anodic compartment of the split cell. At low anodic current densities, at least, one should not expect that anodic current due to cell action would alter the local action current.

Anodic Film Thickness X_a

With suitable approximations for the quantities in Equation 6, as developed in the preceding paragraphs, it became possible to calculate the anodic film thickness X_a:

$$X_a = \frac{IX_c - D \triangle B + L_c X_c}{L_a} \qquad (9)$$

To arrive at experimental values, both the anodic and cathodic probes were allowed to corrode freely to a given penetration, after which the probes were connected to form a cell.

Table 4 illustrates typical data in these experiments. The anodic film thickness data fell onto the same curve as cathodic film thickness data (Figure 9). The processes involving dissolved oxygen were apparently the same at each electrode.

Calculation of Cell Current

Equation 6 permits cell current to be calculated, for the case of 1:1 ratio of anodic: cathodic area since all terms are known or can be estimated by the methods developed in previous paragraphs. A series of runs were made with various solutions in which the actual cell current was compared with the calculated current. Figure 10 shows the results of the experiments. The agreement, while not perfect, supports the validity of the equation.

Calculation of Local Action Current at Anode from Film Thickness Data

Further proof of the diffusion control of local action at the anode can be obtained by comparing calculated local action with actual corrosion current. From Equation 6, L_a, the local action term may be found:

$$L_a = \frac{IX_c + L_c X_c - \triangle DB}{X_a} \qquad (10)$$

Actual corrosion current was determined experimentally by measuring the corrosion rate of "blank" probes in the anodic zone of the cell. The blank corrosion rate measured in μ inches per hour was converted to current in ma/ft^2 by multiplying by a constant derived from Faraday's law, namely, 17.8 for the case of steel.

A number of runs were made to compare L_a with the experimental blank corrosion current. The results, shown in Figure 11, illustrate agreement that is not too bad considering that actual measured corrosion rates are involved in this comparison.

These experiments verifying Equation 6 illustrate the interrelationship between local and long cell action. With dissolved oxygen available, local action will occur at the anodic area of a long cell. This local action increases with increasing cathodic film thickness but decreases with increasing difference in dissolved oxygen between zones.

Effect of pH on Complex Cell Action

As the solution surrounding the anodic part of steel becomes more acidic, the mechanism of the anodic process apparently changes, as evidenced by increased "chunk effect."[8] At the cathode, too, one should expect interesting changes in mechanism with changes in pH. As H^+ ions become more numerous they begin to compete with oxygen as the reducible cathodic material.

Reiller[9] studied the effect of pH on the electrode potential of steel and concluded that there was a large effect in deaerated solutions but a small effect in aerated solutions. His data were applicable to split cells such as were used in the present work. Because of the inherent problems in determining electrode potentials, however, these data are open to question. This was especially true in view of the fact that they predict that there should be no cell action between steel in air-saturated and air-free solutions in a split cell, where both solutions are at or below pH = 2. Actually, current flows quite vigorously in such a cell.

A more realistic but still over simplified study of the effect of pH on cell action was made by Wickert and Wiehr[10] who observed current flow with a split cell apparatus. To eliminate some variables, Wickert and Wiehr determined current output with (1) a steel cathode and an unpolarizable anode (Cd in $CdSO_4$ solution, and (2) a steel anode and unpolarizable cathode (Ni in $NiCl_2$ solution.) They varied the pH of the compartment containing the steel electrode, but maintained dissolved oxygen constant at either a high or low value. Their data indicate cell action increases as the pH is lowered below pH 5 or raised above pH 9.

Introduction of pH as a variable changes a dissolved oxygen cell from simple to complex. The simplified experiments of Reiller and of Wickert and Wiehr do not give a true picture of the complicated nature of such a cell. Both H^+ ions and dissolved O_2 molecules can be reduced; hence steel in a deaerated low pH solution may compete with steel in an aerated neutral solution—with the result that practically no cell action may occur even though drastic conditions are present. Incomplete evidence suggests that, so long as a sorbed oxide film is stable at the cathodic surface, the cell polarity (and to some extent current output) will be controlled by dissolved oxygen. When this film becomes disrupted, the cell is controlled by pH.

An analysis of complex $H^+ - O_2$ concentration cells is in progress and will be reported from this laboratory in a future communication. Below are summarized qualitatively some of the results of complex cell action.

1. Both zones deaerated (simple pH cell). In this condition any action is the result of pH differences in the two zones of the cell. There is no cell action when both zones are oxygen-free and are of pH 5 or above, even if the pH's of the zones are different. (This is in contrast to Reiller's data, which predict that the more basic solution is the anodic zone.)

When the pH of one oxygen-free zone is lowered below pH 5, this zone becomes cathodic. The magnitude of current in such a cell depends upon the pH in the cathodic zone: the lower the pH the greater the cell current. Figure 12 illustrates this effect of cathodic pH on cell current. The cell current is also affected by the pH of the anodic zone but only when this pH is outside the range from pH 5 to 9.

If both zones are deaerated and both are below pH 5, the zone with the lower pH is cathodic. As the pH of the anodic zone approaches that of the cathodic zone, cell current diminishes.

2. Both zones aerated. If both zones are aerated to the same concentration of dissolved oxygen, no cell action occurs until the pH of one zone is lowered to below 5. The situation is similar to the deaerated case with the exception that local action proceeds at both electrodes.

3. One zone aerated, one deaerated. The deaerated zone of pH 3 or lower is anodic so long as the pH of the aerated zone is above about 3. As the pH of the aerated zone is gradually lowered, the cell current remains fairly constant until this value of pH 3 is reached. At this point cell current rapidly reverses and the cell becomes a pH cell with the lower pH zone as cathode. The dissolved oxygen appears to be rendered ineffective as a cathodic or reducible substance at a pH of about 3.

It is possible through careful control of the experimental setup to establish a cell in which the pH cell action exactly counteracts the dissolved oxygen cell action: in such a cell no current flows in spite of gross differences in pH and dissolved oxygen concentrations in the two zones.

From this summary the complexity of O_2—H^+ concentration cells is apparent. In each zone of the cell, dissolved oxygen can vary from 0 to about 9 ppm. The pH can vary from 0 to 14. And other minor but still significant factors like agitation and scale formation can help determine the resulting cell action.

While most of the possible combinations are of academic interest, the overall picture may shed some light on certain corrosion mechanisms.

Effect of Corrosion Inhibitors on Cell Current

Chyzewski and Evans[11] apparently were the first to devise a split cell to study the effect of corrosion inhibitors on cell action. They used dissimilar metal combinations (Fe/Cu or Fe/Zn electrodes) so as to be able to study steel acting as a cathode and as an anode. They found that the presence of inhibitors usually decreased the cell current; some inhibitors affected the current only if placed in the anodic zone and others only if placed in the cathodic zone.

The reactions of inhibitors are of course not instantaneous, so that the split cell provided a convenient means for determining time-cell current relationships. The continuous recording technique and the probes used in the present work simplify the method of Chyzewski and Evans; corrosion rates can be obtained at the same time as cell current, using the same electrodes, and the cell current itself can be continuously recorded.

Runs were made in which steel probes were used in both zones of the cell, and the anodic and cathodic reactions were provided by aeration and deaeration, instead of by dissimilar metals. Cell current was recorded; after it had stabilized, an inhibitor was added to one zone. An effective inhibitor quickly decreased the cell current. Figure 13 summarizes results with several inhibtors.

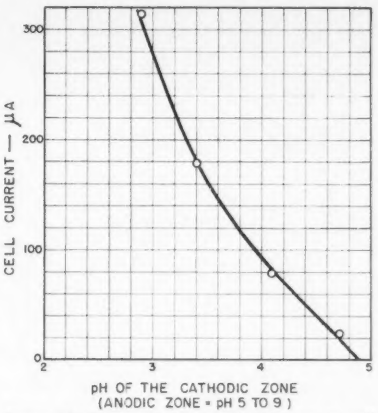

Figure 12—Effect of pH of cathodic zone on cell current. Both zones were deaerated.

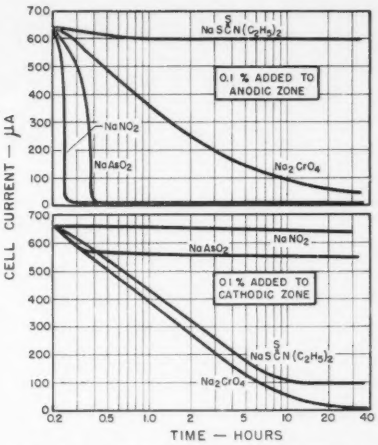

Figure 13—Effect of inhibitors on cell current.

Inhibitor effectiveness can be compared quantitatively by observing the immediate and ultimate (equilibrium) drop in current. Presumably an inhibitor which affects cell current when placed in the anodic zone is an "anodic" inhibitor (i.e., one which interferes with one or more of the processes occurring at the anodic surface).

The split cell does not appear to have been explored fully in connection with studies of inhibitor mechanism; the few experiments reported here of course were merely demonstrative.

Conclusions

A new technique has been developed for studying simple and complex concentration cells. The technique employs a recording zero resistance ammeter and sensitive electrical resistance corrosion probes which permit the measurement of cell current and corrosion rate simultaneously on the same electrodes.

The new technique was used to determine some principles of cell action, namely:

1. In complex cells with variable concentrations of salts and of dissolved oxygen, the oxygen is the current-determining factor.

2. If some oxygen is available initially at the anode of a dissolved oxygen concentration cell, corrosion through local action results in deposition of a film of hydrous ferric oxide which diminishes diffusion of dissolved oxygen. After a matter of hours, the anode behaves as if it is in an oxygen-free environment.

3. In the case of a simple dissolved oxygen concentration cell, cell action can be defined by an equation based on Fick's law of diffusion. Cathodic and anodic diffusion film thicknesses obtained from experimental data were of the order of 0.005 inch.

4. In complex cells where both pH and dissolved oxygen are variable, the dissolved oxygen concentration is current-determining at pH values between 5 and 9. Outside these limits, the cell polarity and current are determined by interaction between the two competing cathodic reactions (the reactions being reduction of H^+ and of O_2).

Brief work is included to illustrate the application of the new technique in the split cell method of studying corrosion inhibitors.

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Any discussion of this article not published above will appear in December, 1960 issue.

Selective Removal of Chromium From Type 304 Stainless Steel By Air-Contaminated Lithium*

By R. E. SEEBOLD, L. S. BIRKS and E. J. BROOKS

Abstract

The corrosive action of high-purity and air-contaminated lithium on Type 304 stainless steel has been studied in non-isothermal closed systems in which maximum and minimum temperatures were 1500 F and 800 F. Chromium is selectively removed to depths of 10 microns from the surface of stainless steel by air-contaminated lithium at 1500 F and remains dissolved in the lithium where it is soluble to the extent of at least 25 percent. The other steel constituents are mass transferred in their original relative proportions and deposited as strongly magnetic dendrites. The preferential leaching of chromium is proposed as the initial step in the corrosion of stainless steel by air-contaminated lithium. 6.25

Introduction

IN THE recent past a great deal of interest has developed in the use of liquid metals as heat exchange media.[1] The major problem, particularly for temperatures near 1500 F, has been one of locating a suitable container material. To be ideally suitable a container material should be inert to the liquid metal. Although in practice no such materials have been found,[2, 3, 4, 5] various types of steels have been suggested and used, purely on the basis of their commerical availability.

The results described here were obtained in unique laboratory systems under duplicable controlled conditions. The apparatus was such that conditions existing at 1500 F in the lithium-stainless steel system could easily be "frozen" for study by x-ray, chemical, and metallographic analysis at room temperature. No complicated parts such as bearings, pump impellers, valve stems and seats, or packings were included in the apparatus, and no piece of apparatus which came into contact with either molten lithium or hot stainless steel was involved in more than one experiment. The complete system from each experiment was available for chemical and physical analyses.

It is felt that the results obtained represent minimum lithium melt-metal reactions and not those resulting from special conditions (i.e., stresses and strains on bearing surfaces, high-velocity erosion, multi-metal couples, and thermal stresses or shock.)

Experimental Procedures

Type 304 stainless steel tubes, closed by heli-arc weldment at the lower end and by an O-ring seal at the upper end were charged respectively with high-purity lithium under helium atmosphere, high-purity lithium under air, and long-time air-contaminated lithium under air. The tubes were 24 inches long with an ID of 0.875" and a wall thickness of 0.063". Fifty-five grams of lithium was the usual charge which, under operating conditions, filled 12 inches of the tubing.

Original loading of the high-purity lithium into the tubes was done by the Maywood Chemical Works, Maywood, New Jersey. The lithium was their best grade having a "nil" content of chloride, oxygen less than 100 ppm, and nitrogen less than 10 ppm. Loading of the air-contaminated lithium was done in the authors' own dry box, as was the admitting of air into certain of the tubes that had been loaded at Maywood.

★ Submitted for publication October 5, 1959.

The loaded tubes were placed in individual furnaces which enclosed the lower four inches of the tubes. Seven Pt/Pt-13 percent Rh thermocouples fastened in two-inch steps up the external wall of each tube provided the furnace control and with electronic recorders kept records of the thermal gradient existing in the lithium-containing portion of the tubes. During operation at temperature the tubes were inclined 45 degrees since preliminary experimentation had shown that smooth convective flow of the lithium obtained at this angle. Figure 1 shows a typical tube in operating position.

At the completion of each corrosion experiment the tube was cooled rapidly and then radiographed to determine the exact position and extent of any mass transfer deposit. All mass transfer deposits occurred within the 800 F to 1000 F zone. This zone was never the coolest portion of the system.

Following radiography each tube was thoroughly cleaned externally and then, using the radiograph as a guide, was sectioned. A tubing cutter was used to assure freedom from small steel particles. Each section of interest was then submerged in anhydrous methyl alcohol which removed the lithium by chemical reaction. No water or hydrates were allowed to enter into the reaction since preliminary experimentation had shown that when hydrates were present, chromium that was present in a separate phase was precipitated as chromic hydroxide $Cr(OH)_3$ which was subsequently confused with the actual metallic mass transfer deposit. By employing anhydrous methyl alcohol this same chromium, which formed $Cr(OH)_3$ in the presence of hydrates, was completely solubilized as Cr^+ to yield a yellow solution.[6] Further experimentation indicated that finely divided metallic chromium did not yield Cr^{+6} when included in the lithium-methyl alcohol reaction.

Metallographic examination disclosed the extent and general type of corrosive action and the physical appearance of the metallic mass transfer deposit. The electron probe microanalyzer[7, 8] yielded quantitative chemical analyses of selected metal areas as small as 1 micron in diameter, thus allowing more accurate small-scale analysis than ever before obtained on corrosion specimens. Chemical analyses gave the gross chemical composition of both metallic deposits and lithium-metal solutions.

General Observations

In those experiments where high-purity lithium was contained under helium atmosphere there was only slight mass transfer action after 720 hours at 1500 F. Spectrochemical analysis indicated that the mass transfer deposit was composed of all the stainless steel constituents. Metallographic examination of the furnace zone of the container showed only mild intergranular penetration to a depth of no more than one grain diameter. Reaction of the mass transfer deposit zone lithium with anhydrous methyl alcohol and subsequent chemical analysis indicated 0.1 percent of hexavalent chromium was present in the lithium. No chromium was found at any other location in the tube.

When high-purity lithium was contaminated with 0.36 percent air the mass transfer deposit after 72 hours at 1500 F was copious enough to virtually bridge the tube diameter. The metallic deposits were highly branched strongly ferromagnetic dendrites. Metallographic examination of the tubing showed moderate intergranular penetration to a depth of slightly more than one grain diameter in the furnace zone. Chemical analysis revealed a concentration of 4.6 percent chromium in the lithium in the immediate vicinity of the mass transfer deposit. Sixteen and nine-tenths percent chromium was found in the cooler portion of the lithium beyond the deposit zone. This chromium was all soluble as Cr^{+6} in methyl alcohol.

The experiments carried out with long-

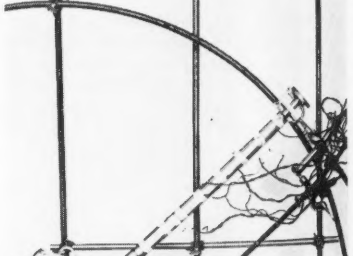

Figure 1—Corrosion tube in operating position showing furnace and thermocouple positions.

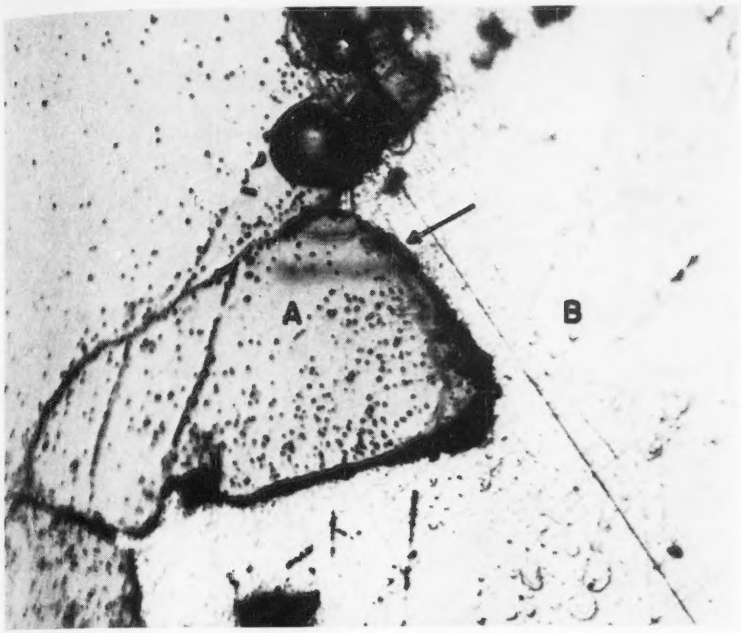

Figure 2—Cross-sectional area of a typical electron probe specimen showing: A. Corroded Type 304 stainless steel; B. Supporting silver electroplate. Arrow indicates electron beam contamination traces. Approximately 750X.

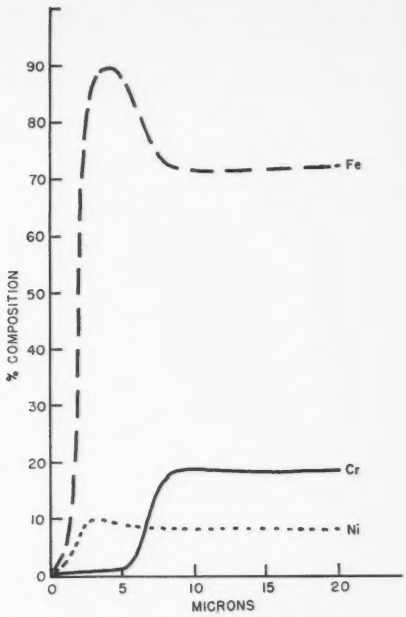

Figure 3—Chromium depletion of Type 304 stainless steel by air-contaminated lithium at 1500 F.

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time air-contaminated lithium yielded results which were different only in degree of mass transfer action when compared with those of 0.36 percent air contamination. Here complete plugging of the tubes over a distance of 1½ inches occurred in 48 hours at 1500 F. The mass transfer deposits were very strongly ferromagnetic dendrites. Chemical analysis revealed the composition range was:

Iron	85-86 percent
Nickel	7-10 percent
Chromium	0.02-2.0 percent
Manganese	4-7 percent
Cobalt	1.0-1.5 percent

Alcohol reaction and subsequent chemical analysis showed the chromium content of the lithium to be 12 percent within the deposit zone and 25 percent in the cooler region beyond the deposit zone.

Electron Probe Results

The role of chromium in the lithium-stainless steel system has been largely neglected by corrosion researchers. The authors' observations indicated that there is a reaction between air-contaminated lithium and chromium, which has not previously been reported. The electron probe microanalyzer was used to examine and quantitatively analyze container sections and metallic mass transfer deposit taken from corrosion experiments involving air-contaminated lithium.

The mass transfer deposit specimens were prepared for analysis by normal metallographic techniques of mounting and polishing. The container sections were heavily electroplated with silver before mounting in order to support the stainless steel during cross-sectional polishing and to eliminate edge rounding.

Electron probe analyses indicated that the mass transfer deposits were homogeneous in iron and nickel on a micron scale. Similar analysis on corroded tubing sections showed that chromium had been preferentially removed from the corroded steel surface to a depth of ten microns. Figure 2 shows a typical cross-sectional area of corroded steel tubing. The arrow points out the contamination trace left by the electron beam during analysis. Figure 3 shows the concentration of chromium, iron, and nickel as functions of distance from the corroded steel surface. All analytical results obtained by use of the electron probe microanalyzer were acquired by simultaneous analysis for all of the elements in question.

Conclusions

In every instance where mass transfer deposition occurred the reaction of the lithium matrix surrounding the deposit with anhydrous methyl alcohol produced a true solution of hexavalent chromium. Electron probe analyses showed that mass transfer deposits were homogeneous on a micron scale; therefore, the chromium

could not have been directly associated with the deposit but must have been present as a separate phase. Further electron probe analysis has shown that chromium is preferentially removed from the surface of Type 304 stainless steel by air-contaminated lithium at 1500 F. The amount of mass transfer occurring per unit time in a Type 304 stainless steel-lithium system operating at 1500 F is dependent upon the degree of air contamination of the lithium. Previous investigators[9] have indicated that nickel is preferentially leached from stainless steels by lithium at 1830 F; however, no indication of this action was noted in this investigation.

In the practical use of lithium in any metal system operating at 1500 F, air contamination of the system presents the greatest problem. Experimental work indicates that deterioration of stainless steel occurs primarily in conjunction with air contamination of the lithium and that this deterioration proceeds through the selective leaching of chromium from the steel. Forced-convection nonisothermal systems would be expected to circulate chromium in solution with the lithium while heavy mass transfer deposits of ferromagnetic iron-nickel alloy formed in cool regions. Steels containing chromium are not recommended for use in lithium systems where air contamination is possible.

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Any discussion of this article not published above will appear in December, 1960 issue.

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SCHEDULED FOR PUBLICATION IN OCTOBER CORROSION

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Zinc as a Self-Regulating Galvanic Anode for Ship Hulls, by J. A. H. Carson

Translation—A Contribution to the Explanation of Intergranular Corrosion of Chromium-Nickel Steel, by V. Cihal and M. Prazak (Translation by F. R. Charvat).

Comptability of Materials With Unsymmetrical Dimethylhydrazine Rocket Fuel, by Paul Derr and Charles W. Raleigh

Corrosion in a Large Diethanolamine Refinery Scrubbing System, by K. L. Moore

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Estimating the Cost of Corrosion in Refinery Crude Units, by N. J. Landis

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Chromium Electroplates for Corrosion Protection of Stressed AISI 410 in High Temperature, High Purity Water, by Henry Suss

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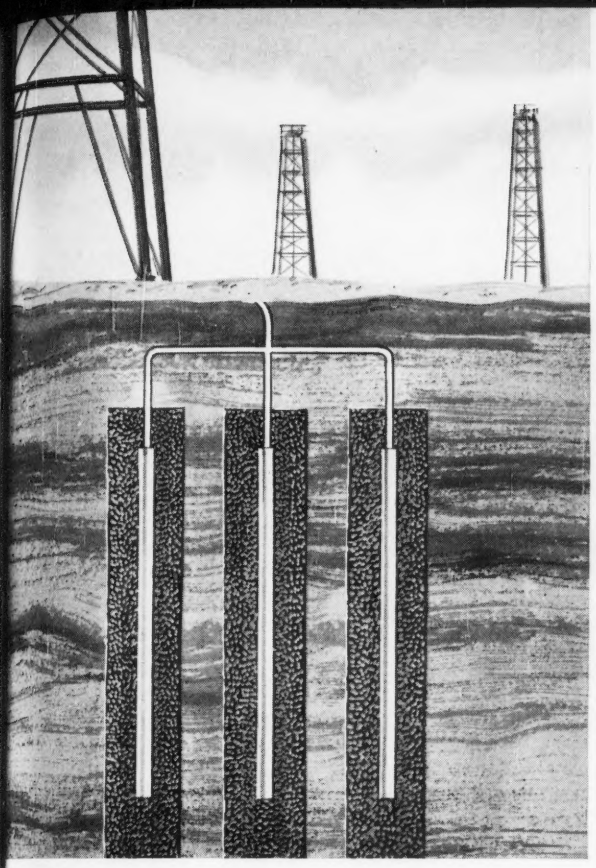

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